

Nano-magnetic-iron Oxides@choline Acetate as a Heterogeneous Catalyst for the Synthesis of 1,2,3-Triazoles

Abolfazl Mohammadkhani¹ · Akbar Heydari¹

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Abstract

In this research, four cholines supported on core–shell iron oxides, $Fe_2O_3@MgO@Ch.OAc$ (choline acetate), $Fe_2O_3@MgO@Ch.OH$ (choline hydroxide), $Fe_3O_4@Ch.OAc$, $Fe_3O_4@Ch.OH$, were synthesized. The synthesized catalysts were tested in 1,2,3-triazoles synthesis by the reaction of nitromethane, aldehyde, and benzyl azide in EtOH as a green solvent. Among four synthesized heterogeneous catalysts, the $Fe_2O_3@MgO@ch.OAc$ showed superior catalytic activity for the reaction and afforded the desired triazoles in good isolated yields under mild reaction conditions.

Graphic Abstract



Keywords 1,2,3 triazoles \cdot Heterogeneous catalyst \cdot Choline hydroxide \cdot Choline acetate \cdot Fe₂O₃/MgO@Ch.OAc

Akbar Heydari heydar_a@modares.ac.ir

Abolfazl Mohammadkhani m_abolfazl@modares.ac.ir

¹ Chemistry Department, Tarbiat Modares University, PO Box:14155-4838 Tehran, Iran

1 Introduction

The triazole derivatives attracted the attention of scientists in the early 1980s [1]. Their derivatives have exhibited important biological activities such as anti-cancer [1], anti-HIV [2], Src-kinase inhibitors [3], anti-microbial [4], anti-allergic [5], and antifungal [6]. They have numerous applications in the industry as fluorescent whiteners, dyestuffs, photo stabilizers of polymers, corrosion inhibitors, photographic photoreceptors, and optical brightening agents [7, 8]. Therefore, some strategies have been introduced for their synthesis such as the azide-alkyne huisgen-cycloaddition reaction [9–15], and the reaction of enamines and azideregents^[16]. One of the attractive synthetic methods is the three-component reaction of aldehydes, nitromethane, and azide derivatives. With the development of 'cascade reactions' as a wonderful tool to operates plenty of organic syntheses, some scientific teams have been focus to improve cascade methodologies for instance three-component reaction of aldehydes, nitromethane, and azide derivatives which interact initially to generate an intermediate that reacts further to furnish the final product, onepot, without eliminating intermediate and separation [17].

Since the interesting work by Abbott and coworkers on using deep eutectic solvent (DES) as a green ion liquid in the 2003 year, sscientists have used different deep eutectic solvents to synthesize new drug candidates and heterocyclic compounds such as coumarins [18], indoles [19], and 2-aminothiazoles [20]. The use of DES as a green, inexpensive, biodegradable, non-flammable, and non-volatile compound has reported in various fields such as organic reaction as catalyst or solvent, renewable energy storage, bioengineering, biotechnology, medicinal chemistry, biomass valorization, extraction, and gas separation [21–29]. The most widely spread DESs are produced by blending a hydrogen bond acceptor (HBA), exemplified by an inexpensive quaternary ammonium salts such as choline chloride (ChCl, included in the so-called vitamin B4) or other cholines, with a hydrogen bond donor (HBD) such as sugars, eggs, organic and amino acids, urea or glycerol [30]. These days plenty of publications have been reported for the organic synthesis regarding the progressive organo-catalysts coordinated to inorganic solids, due to the economical aspect, and environmental dimension [31, 32]. It sounds important to examine the activity of coordinated cholines to Lewis acid magnetic surface, as a heterogeneous multi-functional catalyst for the modification purposes [33].

Herein, Fe₂O₃/MgO@Ch.OAc (choline acetate), Fe₂O₃/MgO@Ch.OH (choline hydroxide), Fe₃O₄@Ch.OAc, and Fe₃O₄@Ch.OH have been evaluated as heterogeneous systems for the synthesis of 1,2,3-triazoles by the three-component reaction of aldehydes, benzyl azide, and nitromethane in EtOH as a green solvent with a low health and environmental hazard[34]. Lewis acidity capability, low toxicity, high surface area, simple preparation, capacity for surface functionalization, and high recovery with an external magnetic field are the advantages of magnetic nanoparticle supports [35–37].



Scheme 1 Schematic diagram of catalysts preparation





Fig.1 FT-IR spectrum of preparation of $Fe_2O_3@MgO$ (A), $Fe_2O_3/MgO@Ch.OAc$ (B), and $Fe_2O_3/MgO@Ch.OH$ (C) $Fe_3O_4@Ch.OH$, and $Fe_3O_4@Ch.OAc$ (D)

2 Materials and Methods

2.1 Chemicals and Materials

All chemicals were purchased from Merck, Aldrich, or Fluka were used without further purification. The NMR spectra were recorded on a BRUKERDRX-300AVANCE Advance spectrometer. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with an FID detector and Rtx®-1 capillary column. Melting points of products were measured with an Electrothermal 9100 apparatus and were uncorrected. IR spectra (with spectroscopic grade KBr) were recorded by Nicolet IR100 instrument and the spectra were obtained over the region 400–4000 cm⁻¹ The magnetic measurement experiments were obtained by using a vibrating magnetometer/alternating gradient force magnetometer (MD Co., Iran, www. mdk-magnetic.com). X-ray diffraction pattern (XRD) was determined by a Philips X-Pert 1710 diffraction meter. Energy-Dispersive X-ray spectroscopy (EDX) spectra and



Fig. 1 (continued)

Field Emission Scanning Electron Microscopy (FE-SEM) images were recorded on Tescan MIRA3 FE-SEM (http://www.tescan.co.kr/product/em/em02). Thermal Gravimetry-Analysis (TGA): Netzsch:- TGA 209 F1.

2.2 General Produce

2.2.1 Preparation of Choline Acetate

A mixture of choline chloride (1 mol) and sodium acetate (1 mol) was refluxed in methanol (500 mL) for 12 h. As a result of inion exchange, the sodium chloride settled as sediment. The cooled bulk was filtered and methanol solution was evaporated under reduced pressure to afford the choline acetate.

2.2.2 Preparation of Choline Hydroxide

A mixture of choline chloride (1 mol) and sodium hydroxide (1 mol) was refluxed in methanol (500 mL) for 12 h. As a result of inion exchange, the sodium chloride settled as sediment. The cooled bulk was filtered and methanol solution was evaporated under reduced pressure to afford the choline hydroxide.

2.2.3 Preparation of Fe₂O₃@MgO

 Fe_3O_4 nanoparticles were prepared by heating a mixture of 100 mL aqueous solution of $FeCl_2$ ·4H₂O (5 mmol),and $FeCl_3$ ·6H₂O (10 mmol) to 85 °C. Then, ammonia (20 mL 27 wt %) was added dropwise into the above solution under



Fig. 2 TGA of $Fe_2O_3/MgO@Ch.OAc$ (blue line), $Fe_2O_3/MgO@Ch. OH$ (gray line), $Fe_3O_4@Ch.OAc$ (orange line), and $Fe_3O_4@Ch.OH$ (yellow line),

stirring to reach pH = 10-11. After stirring for 1 h at room temperature and the resulting black dispersion was heated to reflux for 1 h. brown precipitate was separated by an external magnet, and then washed several times with deionized water until the effluent solution pH was neutral. The particles were also washed with ethanol and suspended in ethanol. MgNO₃ or MgCl₂ (5 mmol) with an excess of water (1:20) was added to the ethanol suspension of magnetite nanoparticles under sonication. The reaction mixture was kept under sonication for 1 h and heated, subsequently stirred for 12 h, at 70 °C under stirring.particles separated by an external magnet washed once with ethanol, and recovered by an external magnet. The obtained powder (magnetite nanoparticles coated with magnesium hydroxide) was calcined in air at 400 °C for 4 h.

2.2.4 Preparation of Fe₂O₃/MgO@Ch.OH

A mixture of Fe_2O_3/MgO (0.5 g), EtOH (3 mL), and choline hydroxide (4 mmol) were stirred for 15 min at 25 °C. Then, the mixture was stirred at 90 °C for 12 h. The Burnt brownorang catalyst was separated by potent magnet decantation. The catalyst was washed with EtOH, and acetone dried at 50 °C for 12 h.

2.2.5 Preparation of Fe₂O₃/MgO@ Ch.OAc

A mixture of Fe_2O_3/MgO (0.5 g), EtOH (3 mL), and choline acetate (4 mmol) were stirred for 15 min at 25 °C. Then, the mixture was stirred at 90 °C for 12 h. The Burnt brownorang catalyst was separated by potent magnet decantation. The catalyst was washed with EtOH and acetone dried at 50 $^{\circ}$ C for 12 h.

2.2.6 Preparation of Fe₃O₄@Ch.OH

A mixture of Fe_3O_4 (0.5 g), EtOH (3 mL), and choline hydroxide (4 mmol) were stirred for 15 min at 25 °C. Then, the mixture was stirred at 90 °C for 12 h. The Burnt brownorang catalyst was separated by potent magnet decantation. The catalyst was washed with EtOH and acetone dried at 50 °C for 12 h.

2.2.7 Preparation of Fe₃O₄@ Ch.OAc

A mixture of Fe_3O_4 (0.5 g), EtOH (3 mL), and choline acetate (4 mmol) were stirred for 15 min at 25 °C. Then, the mixture was stirred at 90 °C for 12 h. The Burnt brownorang catalyst was separated by potent magnet decantation. The catalyst was washed with EtOH and acetone dried at 50 °C for 12 h.

2.2.8 General Procedure for the Synthesis of 1,2,3 triazoles

A mixture of catalyst (100 mg), aldehyde (2.5 mmol), nitromethane (2.5 mmol), benzyl azides (2.5 mol) in EtOH (2 mL) were stirred at 85 °C. After completion of the reaction (TLC), the magnetic catalyst was separated by an external magnet. The reaction solution was diluted with water (2 mL) and chloroform (2×2 mL) and water. The organic layer was separated and then concentrated under reduced



Fig. 3 SEM images of Fe₂O₃/MgO@Ch.OAc (A), Fe₂O₃/MgO@Ch.OH (B) Fe₃O₄@Ch.OAc (A), and Fe₃O₄@Ch.OH (B^{*})

pressure. The pure product was obtained by recrystallization with $CHCl_3$: n-Hexane (1:3).

2.2.9 General Procedure for Synthesis of Benzyl Azide

A mixture of Benzyl halide(1 mmol), DMF (2 ml), and sodium azide(1.5 mmol), were stirred at 85 °C for 5 h. After completion of the reaction (TLC), the magnetic catalyst was separated by an external magnet. The reaction solution was diluted with water (2 mL) and chloroform (2×2 mL) and water. The organic layer was separated and then concentrated under reduced pressure.

3 Results and Discussion

3.1 Characterization of Catalyst

The process for the synthesis of $Fe_2O_3/MgO@Ch.OAc$, $Fe_2O_3/MgO@Ch.OH$, $Fe_3O_4@Ch.OAc$, and $Fe_3O_4@Ch.OH$



Fig. 4 EDS images of Fe₂O₃/MgO@Choline acetate (A), Fe₂O₃/MgO@Ch. OH (B), Fe₃O₄@Ch.OAc (A') and Fe₃O₄@Ch.OH (B')



Fig. 5 VSM curve of Fe_3O_4 , $Fe_2O_3@MgO$, $Fe_2O_3/MgO@$ Ch.OAc $Fe_2O_3/MgO@Ch.OH$, Fe_3O_4 , @Ch.OAc, and Fe_3O_4 , @ Ch.OH

are illustrated in Scheme 1. The Fe_3O_4 was synthesized according to the previous report [38]. The Fe_3O_4 @Ch.OAc or Ch. OH-composite was synthesized by the reaction of Fe_3O_4 magnetic powder and choline acetate or hydroxide in ethanol at 85 °C for 8 h. The catalyst was separated and washed with ethanol and acetone and dried in the oven at 60 °C. The Fe_2O_3 @MgO was obtained by the reaction of Fe_3O_4 with magnesium nitrate and ammonium hydroxide (27%Wt) at 70 °C for 12 h. The magnetic powder was separated and heated in a furnace until 400 °C for 4 h to afford the fine orange-brown powder. In the next step, choline acetate or choline hydroxide and Fe₂O₃@MgO were refluxed in ethanol at 85 °C for 12 h to afford the Fe₂O₃@MgO@Ch.X (X=OH or OAc).

The synthesized catalysts were characterized by FT-IR, thermos-gravimetric analysis (TGA), field emission



Fig. 6 XRD pattern of Fe₂O₃/MgO(A-blue line) Fe₂O₃/MgO@Cholines (A red line)



Fig. 7 XRD pattern Fe₃O₄(A-red line) Fe₃O₄@Cholines (B black line)

scanning electron microscopy (FESEM), energy-dispersive x-ray spectroscopy (EDS), vibrating sample magnetometer (VSM), and x-ray diffraction (XRD) measurements.

The FT-IR spectra of the choline acetate, choline hydroxide, Fe_3O_4 @cholines, and Fe_2O_3 @MgO@cholines are shown in Fig. 1 [33]. The FT-IR spectrum of choline acetate shows characteristic bands at 1738 and 1411 cm⁻¹ for the C=O group of acetate and the C-N bond,

respectively (Fig. 1B-red line) [39]. The spectra of choline hydroxide show characteristics bonds at 3421, 1959, and 1357 and 1054 cm⁻¹ assigned to the –OH, C-H sp³, C–N, and C–O groups, respectively [40, 41] (Fig. 1C-green line). The FT-IR spectra of all catalysts show broadband at 540–580 cm⁻¹ for the stretching vibration of the Fe–O bonds assigned to the spinel form of iron oxide (Fig. 1D) [42]. The peak at 1621 cm⁻¹ for the O–H bond of Fe₃O₄

Table 1 Optimization of 1,2,3-triazoles



Entry	Cat	solvent	Base	Temperature (°C)	Yield (%)*
1	Fe ₃ O ₄	EtOH	_	85	Trace
2	Fe ₂ O ₃ @MgO	EtOH	_	85	Trace
3	Fe ₂ O ₃ /MgO@Ch.OAc	EtOH	-	85	72%
4	Fe ₂ O ₃ /MgO@Ch.OH	EtOH	_	85	67%
5	Fe ₃ O ₄ @Ch.OAc	EtOH	-	85	42%
6	Fe ₃ O ₄ @Ch.OH	EtOH	-	85	47%
7	Fe ₂ O ₃ /MgO@Ch.OAc	EtOH	_	25	Trace
8	Fe ₂ O ₃ /MgO@Ch.OAc	EtOH	-	60	%35
9	Fe ₂ O ₃ /MgO@Ch.OAc	MeCN	-	85	%34
10	Fe ₂ O ₃ /MgO@Ch.OAc	Toluene	-	85	Trace
11	Fe ₂ O ₃ /MgO@Ch.OAc	H ₂ O	-	85	Trace
12	Fe ₂ O ₃ /MgO@Ch.OAc	MeOH	-	85	%56
13	Fe ₂ O ₃ /MgO@Ch.OAc	EtOH/H ₂ O (1/5)	-	85	%25
14 ^a	Fe ₂ O ₃ /MgO@Ch.OA	EtOH	-	85	59%
15 ^b	Fe ₂ O ₃ /MgO@Ch.OAC	EtOH	_	85	75%
15	Fe ₂ O ₃ /MgO@Ch.OAC	EtOH	КОН	85	39%
16 ^c	Fe ₂ O ₃ /MgO@Ch.OAC	EtOH	NaOAC	85	78%
17 ^d	Fe ₂ O ₃ /MgO@Ch.OAC	EtOH	K ₂ CO ₃	85	89%
18 ^d	Fe ₂ O ₃ /MgO@Ch.OAC	EtOH	Na ₂ CO ₃	85	86%

Benzaldehyde (2.5 mmol), nitromethane (2.5 mmol), benzylazide (2.5 mmol), Cat: 100 mg, for 5 h

*Isolated yield

 $^{a}Cat = 70 \text{ mg}$

^bCat = 140 mg, the reaction conversion is 100%

^cReaction time = 4.5 h

^dReaction time = 3.5 h

[43] (Fig. 1A), shifted to 1609 cm^{-1} [44] (Fig. 1D) which confirms the coordination of choline acetate and hydroxide (Fig. 1D-green and red). The FT-IR peak of choline acetate in Fe₂O₃/Mg@Ch.OAc (1642 cm⁻¹) and choline hydroxide in Fe₂O₃/Mg@Ch.OH (1664 cm⁻¹) shift to 1607 and 1632 cm⁻¹, respectively (Fig. 1 blue-B and red-C). It is due to the surface chelation of Fe₂O₃/MgO to organic groups [44] (Fig. 1B, C).

The TGA was further used to investigate the composition and thermal resistance of the catalysts (Fig. 2). The TGA curve of the Fe₂O₃/MgO@ Ch.OAc shows a weight loss at ~ 100 °C which is associated with the physically adsorbed H₂O. The 10% weight loss at 220–620 °C is related to the decomposition of organic groups from the Fe₂O₃/Mgo@ Ch.OAc. Thermal analysis shows that the catalysts have thermal stability until 200 °C (Fig. 2). Also, 17% weight loss of Fe₂O₃/MgO@ Ch. OH initiated from 170 °C and continued to 620 °C which showed that the catalysts have thermal stability until 170 °C (Fig. 2). As can be seen from Fig. 2, the TGA cures of the Fe₃O₄@Ch.OA and Fe₃O₄@Ch.OH showed weight losses about 13% and 15%, respectively.

The surface morphology of fresh $Fe_2O_3/MgO@Ch.OAc$, $Fe_2O_3/MgO@Ch.OH$, $Fe_3O_4@Ch.OAc$, and $Fe_3O_4@Ch.OH$ nanocomposites were detected by FE-SEM separately (Fig. 3). They show the formation of spherical particles with an average size of 23, 38, 26, 28 nm, respectively. The EDS analysis of $Fe_2O_3/Mg@cholines$ and $Fe_3O_4@cholines$

 Table 2
 Screening of the derivatives 1,2,3triazoles synthesis



Product 4	\mathbb{R}^1	\mathbb{R}^2	Yield (%)*	Yield (%)**	M.P.(°C)	Ref
a	Н	Н	73	86	131–133	[49]
b	Н	4-OMe	70	85	117-119	[50]
c	Н	4-NO ₂	62	76	140-141	[51]
d	Н	4-Br	74	88	150-152	[51]
e	Н	2,4 Cl	69	82	116-117	[52]
f	Н	3-OMe	68	84	84-85	[53]
g	3-Me	Н	70	81	146	[54]
h	4-OMe	Н	74	87	141-143	[55]
i	$4-NO_2$	Н	61	76	168	[56]
j	4-Me	Н	70	84	128-129	[57]
k	4-OMe	4-Me	73	86	149–151	[58]
1	4-Me	4-OMe	74	88	133–134	[59]
m	4-Me	4-Br	70	83	202-203	[51]
n	4-Me	3-OMe	74	85	167	[<mark>60</mark>]

*isolated yield without base /**isolated yield in the presence of K2CO3

(Fig. 4) exhibited the presence of their main elements in the composites.

The magnetic hysteresis loop measurements of the Fe₂O₃/MgO@Ch.OAc, Fe₂O₃/MgO@Ch.OH, Fe₃O₄@Ch.OAc, and Fe₃O₄@Ch.OH are less than Fe₃O₄ [37] and Fe₂O₃@ MgO [45] (58.5 and 42.6 emus.g-1) and indicate saturation magnetization value of 29.84, 27.7, 46.9, and 45.3, respectively. This diminution of MS value can indicate the change of Fe₃O₄ into γ -Fe₂O₃ during the heating [46] or coating magnesium oxide on iron oxide [45]. The incorporation of cholines on the surface of Fe₃O₄ and Fe₂O₃@MgO may reduce saturation magnetization values (Fig. 5).



Fig. 8 Hot filtration Test

To determine the crystalline structure of the Fe₂O₃/MgO@Cholines, its XRD pattern was studied in a domain of $10^{\circ}-80^{\circ}$. There are not many changes in the XRD pattern of Fe₂O₃@MgO (red line) and Fe₂O₃/MgO@Cholines acetate and hydroxide nano-magnetic (blue line) (Fig. 6). The diffractions at 2 Θ (Cu) = 30, 35.6, 36.8, 42.9 53.8, 57.2,62.2 and 62.7 can be assigned to the (220), (311), (222),(400), (442), (511), (440), and (531), crystalline planes of cubic lattices structure of Fe₂O₃ (JCPDS card No. 39–1346 [46]). Moreover, the diffractions at 2 Θ (Co) = 21.08, 50.3 and 73.8 can be ascribed to MgO (JCPDS 4–829) [47, 48] (Fig. 6).

The XRD pattern of the Fe_3O_4 and Fe_3O_4 @Cholines (Fig. 7) show diffraction peaks at around $2\Theta(Cu) = 30.3^\circ$, 35.7° , 43.3° , 53.7° , 57.3° , and 62.9° which can be assigned to the (220), (311), (400),(422), (511), and (440) crystalline planes of cubic lattices structure of Fe_3O_4 (JCPDS19–62).

3.2 The Catalytic Activity of the Catalysts

After synthesized and characterization the catalysts, their catalytic activity was tested in 1,2,3-triazoles synthesis. The reaction of benzaldehyde **1a**, nitromethane **2**, and benzyl azide **3a** was chosen as a model reaction. First, the model reaction was carried out using Fe_3O_4 , Fe_2O_3 @MgO, Fe_2O_3 /MgO@Ch.OH, Fe_2O_3 /MgO@Ch.OAc, Fe_3O_4 @Ch.OAc,

Fig. 9 Recyclability of Fe₂O₃/ MgO@Ch.OAc



Fig. 10 XRD of reuse $Fe_2O_3/MgO@Ch. OAcA:$ the first step reuse and E: the last step of reuse





Fig. 11 SEM images of reuse Fe₂O₃/MgO@Ch.OAc



Fig. 12 VSM of reuse Fe₂O₂/MgO@Ch.OAc

 Table 3 compares the efficiency of various methods for synthesis of 1,2,3,triazoles

and Fe₃O₄@Ch.OH as a catalyst in EtOH under reflux conditions for 5 h (Table 1, entries 1-6). As can be seen in Table 1, the reaction in the presence of the $Fe_2O_3/MgO@$ Ch.OAc afforded a higher isolated yield (72%, Entry 3). Therefore, the Fe₂O₃/MgO@Ch.OAc was selected as a superior catalyst for further studies. The reaction was tested at lower temperatures. It was found that the lower reaction temperatures led to lower yields (entries 7 and 8). The various solvents such as H₂O, H₂O/EtOH, MeOH, MeCN, and toluene were investigated (entries 9-13). It was found that the superior solvent was EtOH (entry 3). The amount of catalyst was optimized in the reaction (entries 14 and 15). As can be seen in Table 1, the 100 mg of the catalyst produced the desired product in a higher isolated yield (Entry 3). Finally, the role of bases such as KOH, NaOAc, Na₂CO₃ and K₂CO₃ was investigated in the model reaction (entries 15–18). Notably, the reaction in the presence of K_2CO_3 led to a higher isolated yield in a shorter reaction time (entry 17).

Having acquired the optimal conditions in hand, we next intended to explore the scope of the reaction. Various benzyl azides and aldehydes containing electrons donating and electron-withdrawing functionalities were tested in the reaction (Table 2). As can be seen in Table 2, The various substituted benzyl azides could be successfully reacted with nitro styrenes (formed in situ by Henry's reaction of nitromethane and aldehydes) to generate 1,2,3-triazoles in good isolated yields. The proposed mechanism can be found with more details in supporting information.

3.3 Recyclability Heterogeneous Catalyst

After the study of the catalytic activity of the $Fe_2O_3/MgO@$ Ch.OAc, its heterogeneous nature was investigated. First, a hot filtration test was done for the reaction of benzaldehyde 1a, nitromethane 2, and benzyl azide 3a under optimized conditions to test the choline leaching from the heterogeneous catalyst through the reaction. After 1 h, the reaction was

	-	-	-			
Entry	Solvent	Time	Additives	Temperature (°C)	Maximum Yield	Reference
1	DMSO	Overnight	AlCl ₃	70	95%	[61]
2	DMSO	5 min	Cu-Fe ₂ O ₄	120-M.W. ^a ,700w	90%	[17]
4	H_2O	12 h	Cu-Fe2O4	R.T	85%	[62]
5	DMF	10 min	Pd-MCM-41/Na ₂ CO ₃	120	82%	[63]
6	DMSO	45 min	Fe ₃ O ₄ @SiO ₂ @Propyl-HMTA	110	95%	[64]
7	PEG-400	3 h	PEG capped ZnO	100	98%	[65]
8	DMF	30 min	Al-MCM-41/piperidine	80 -M.W ^a	90%	[66]
9	DMF	30 min	sulfated zirconia/ piperidine	80 -M.W ^a	90%	[66]
10	EtOH	5.5 h	Fe ₂ O ₃ /MgO@Ch.OAc	85	70–74%	This work
11	EtOH	3.5 h	Fe ₂ O ₃ /MgO@Ch.OAc/k ₂ CO ₃	85	89%	This work

^aMW microwave

stopped and the catalyst was separated by a magnet. During further heating of the filtrates for 2.5 h, no significant progress was detected (Fig. 8). Then, the recyclability of the catalyst was investigated in the model reactions. The heterogeneous catalyst could be recycled at least five times without significant loss of activity (Fig. 9). The structure of reused catalyst after five runs was investigated by FT-IR (Fig. 1), XRD (Fig. 10), FE-SEM (Fig. 11), and VSM (Fig. 12). All analyses showed that the structure of reused Fe₂O₃/MgO@ Ch.OAc was similar to the fresh catalyst. All results confirm this reaction occurs mainly via a heterogeneous route.

Table 3 compares the efficiency of $Fe_2O_3/MgO@Ch.OAc$ with some reported catalysts in the 1,2,3-triazoles synthesis. It shows that the $Fe_2O_3/MgO@Ch.OAc$ has good catalytic efficiency in mild reaction conditions for the 1,2,3-triazoles synthesis.

4 Conclusions

In this work, four new heterogeneous catalysts, $Fe_2O_3@MgO@Ch.OAc$, $Fe_2O_3@MgO@Ch.OH$, $Fe_3O_4@Ch.OAc$, $Fe_3O_4@Ch.OH$, were synthesized, characterized, and tested in a three-component reaction of benzyl azide, aldehyde, and nitromethane for the synthesis of 1,2,3-triazoles. It was found, the heterogenized $Fe_2O_3@MgO@ch.OAc$ has an efficient catalytic activity for the 1,2,3, triazoles synthesis. The important aspects of the reaction such as its simple operations under mild conditions, compatibility with a wide range of substrates, high atom economy, good yields of the products, recyclability, and leaching-free feature of the catalyst, make this catalytic strategy very attractive and eco-friendly process for the 1,2,3, triazoles synthesis.

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Data Availability The data that supports the findings of this study are available in the supplementary material of this article.

Declarations

Conflict of interest There are no conflicts of interest to declare.

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