Journal of Organometallic Chemistry 897 (2019) 139–147

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Environmentally benign synthesis of pyranopyrazole derivatives by cobalt Schiff-base complexes immobilized on magnetic iron oxide nanoparticles

Behrouz Shaabani*, Hossein Maleki, Jamshid Rakhtshah

Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:
Received 28 April 2019
Received in revised form
14 June 2019
Accepted 22 June 2019
Available online 24 June 2019

Keywords:
Immobilized complexes
Fe_3O_4 nanoparticles
Pyranopyrazoles
Solvent-free

ABSTRACT

In this work, an efficient and straight procedure has been described for one-pot three-component synthesis of pyranopyrazole derivatives in the presence of a new cobalt Schiff-base complex immobilized on silica-coated Fe_3O_4 nanoparticles as a reusable catalyst. This new catalyst was characterized by different techniques, such as Fourier transform infrared (FT-IR), X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma (ICP) and vibrating sample magnetometry (VSM). The described catalyst was efficiently tested in the synthesis of pyranopyrazoles via three-component condensation of different aromatic aldehydes, malononitrile and 3-methyl-1-phenyl-2-pyrazoline-5-one at room temperature with short reaction times, high yields and TON values up to 388. The considered catalyst can be reused several times without loss of its catalytic activity. Finally, we compared the results for the synthesis of desired products in the presence of our nanocatalyst with previously reported catalysts in the literature.

1. Introduction:

Multicomponent reactions (MCRs) are those reactions in which more than two first materials react together to form a single product, contains the ingredient of all the components. MCRs have emerged as a vital field of chemistry and a powerful tool in synthetic organic chemistry [1–3]. These reactions are covering unique features like high selectivity, high yield and synthetic simplicity due to the formation of carbon-carbon and carbon-heteroatom bonds in a single step [4–10].

Pyranopyrazoles are biological active heterocyclic compounds that illustrate a wide range activity like antimicrobial [11], antitumor [12], anticancer [13], anti-inflammatory [14], and also as biodegradable agrochemicals [15]. The synthetic contractual method for preparation of pyranopyrazole derivatives is a three-component reaction of aromatic aldehydes, malononitrile and 3-methyl-1-phenyl-2-pyrazoline-5-one under various conditions and catalysts such as DABCO [16], basic catalysts [17], nanosized magnesium oxide [18], bovine serum albumin [19], imidazole [20], CuO/ZrO_2 [21], ionic liquids [22], ultrasound irradiation [23], aqueous media [24], $H_{14}[NaP_5W_{30}O_{110}]$ [25], and trichloroacetic acid [26].

Over the past two decades, Schiff bases have been playing a pivotal role in chelating the intermediate metals, as well as the main group metals, one of the important features of Schiff bases, are their stability to moisture and high temperature (up to 100 °C) which makes them one dominant type of organic ligands. They can be used as a catalyst in both homogeneous and heterogeneous reactions such as reduction [27], oxidation of organic compounds [28], hydrosilylation of ketones [29] and multi-component reactions [30]. One of the significant disadvantages of homogeneous catalytic systems is the problem of separation and recovery of the catalysts from the reaction media [31–33]. In recent years, many attempts have been made to immobilize Schiff-base complexes on different solid supports such as silica [34,35], carbon [36] and metal oxides [37] to solve these problems. Recently magnetic nanoparticles (MNPs) have been widely considered for the immobilization of homogeneous catalysts because of their unique properties likes chemical stability, strong magnetization, high activities and easy recovery in heterogeneous catalytic processes [38-41]. Iron oxide nanoparticles are unstable under acidic conditions, and the magnetic core is usually protected with an outer shell such as silica [42,43] or polymers [44]. Silica is an adequate candidate, which has

---

* Corresponding author.
E-mail address: Shaabani.b@gmail.com (B. Shaabani).

https://doi.org/10.1016/j.jorganchem.2019.06.030

an excellent chemical affinity and thermal stability. An advantage of the silica coating is terminating of the surface with abundant Si—OH bond which facilitates the immobilization of desired compounds on magnetic nanoparticles.

In continuation of our efforts in the field of synthesis immobilized Schiff-base complexes on different supports likes MNPs [45,46] and MWCNTs [47,48], we report the synthesis and characterization of new cobalt Schiff-base complexes supported on Fe_3O_4 nanoparticles as an efficient and recoverable catalyst in the synthesis of pyranopyrazole derivatives(Scheme 1).

2. Experimental

2.1. Synthesis of magnetite Fe_3O_4 nanoparticles

The Fe_3O_4 NPs were prepared by chemical co-precipitation technique according to a previously published method [49]. A mixture of $FeCl_3\cdot6H_2O$ (2 mmol) and $FeCl_2\cdot4H_2O$ (1 mmol) in deionized water was added to a three-necked round-bottomed flask (250 mL). The mixture was stirred for 10 min at 80 °C, then, 15 mL of concentrated ammonia (25%) was added rapidly to the solution. The black mixture was stirred under N_2 atmosphere for another 2 h then cooled to room temperature. The black precipitate was separated magnetically and washed several times with water until the pH of the runoff was around 7 and then, dried at 60 °C under vacuum.

2.2. Synthesis of silica-coated iron oxide nanoparticle (Fe_3O_4@SiO_2)

The Fe_3O_4@SiO_2 nanoparticles were prepared according to the Stober method [50]. For coating magnetite nanoparticles with a layer of silica, synthesized nanoparticles (1.0 g) were dispersed by ultrasonic vibration in a mixture of 100 mL of ethanol, 10 mL of deionized water and 4 mL of tetraethylorthosilicate (TEOS). In the following, 2.5 mL of 25 wt% concentrated aqueous ammonia solution was injected dropwise into the reaction mixture, and the pH value was controlled in the range $11 \leq pH \leq 12$. After stirring the mixture for 6 h at room temperature, the brown precipitate was collected from the solution by using an external magnet, and washed several times with ethanol and dried under vacuum.

2.3. Synthesis of magnetite nanoparticles coated by 3-chloropropyltrimethoxysilane (Fe_3O_4@SiO_2@Cl)

1 g of silica coated nanoparticles, synthesized in the previous section, were dispersed in 100 mL ethanol solution of 3-chloropropyltrimethoxysilane (CPTMS) (2.5 mL) under reflux condition and N_2 atmosphere for 12 h. The obtained particles were collected using a magnet and subsequently washed with ethanol three times.

2.4. Synthesis of cobalt Schiff-base complex (CoSB)

A solution of 2-amino phenol (1 mmol, 0.109 g) in absolute EtOH (10 mL) was added dropwise to a stirring solution of 2-pyridine carboxaldehyde (1 mmol, 0.107 g) in absolute EtOH (20 mL) during 10 min at 60 °C. After the addition was completed, the reaction mixture was stirred for 4 h under reflux at 60 °C. The residue was washed with ethanol and dried under vacuum.

2.5. Synthesis of cobalt Schiff-base complex immobilized on silica coated Fe_3O_4 (Fe_3O_4@SiO_2@CoSB)

The as-prepared Fe_3O_4@SiO_2@Cl (1 g) were dispersed by ultrasonic vibration in ethanol solution for 20 min, then the cobalt complex was added to the mentioned solution and stirred at 60 °C under reflux for 24 h. The resulted precipitate was separated from the solution by an external magnet and washed several times with ethanol and dried in the air.

2.6. General procedure for the synthesis of pyranopyrazole derivatives

Fe_3O_4@SiO_2@CoSB as a magnetic nanocatalyst (8 mg) was added to a mixture of aromatic aldehyde (1 mmol), malononitrile (0.066 g, 1 mmol) and 3-methyl-1-phenyl-2-pyrazoline-5-one (0.174 g, 1 mmol) in an ethanolic medium at room temperature. After completion of the reaction which was identified by TLC (*n*-hexane/ethyl acetate: 5/2), the nanocatalyst was recovered magnetically by adding 5 mL ethyl acetate to solve the product and then it was purified via recrystallization from ethanol.

2.6.1. 6-amino-4-(2,3-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 4, entry 10)

^1H NMR (400 MHz, DMSO-d_6): δ_{ppm} 9.42 (s, 1H,-OH), 8.06 (dd, 1H, $J_1 = 8.0$, $J_2 = 6.0$, ArH), 7.90 (d, 2H, J = 4.0, ArH), 7.86 (t, 2H, J = 4.0, ArH), 7.33 (s, 1H, OH), 7.09 (t, 1H, J = 8.0, ArH), 6.73 (d, 1H, J = 8.0, ArH), 6.69 (s, 2H, NH_2), 6.62 (d, 1H, J = 8.0, ArH), 4.51 (s, 1H, –CH), 2.33 (s, 3H, CH_3); ^1H NMR (400 MHz, DMSO-d_6): δ_{ppm} 158.3, 157.3, 148.6, 144.8, 134.5, 134.1, 130.9, 130.5, 129.5, 126.0, 125.8, 122.1, 119.3, 118.2, 114.3, 114.1, 114.0, 57.3, 36.2.

2.7. General procedure for reusing experiments

The reusability of the catalyst was studied in recycling experiments. To regenerate the catalyst, after finishing each run, 3 mL of hot ethyl acetate was added to the reaction mixture and heated to dissolve the product. Then, the nanocatalyst was separated from the reaction mixture by an external magnet and washed with ethanol to reused in the next reaction for eight times.

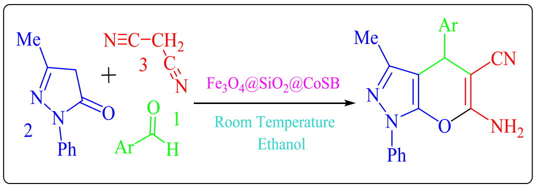
3. Results and discussion:

3.1. Characterization of cobalt Schiff-base complex immobilized on Fe_3O_4 as a heterogeneous catalyst

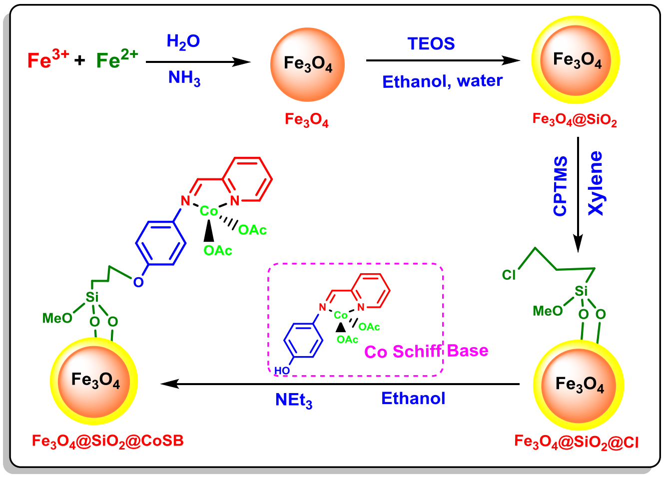
A new cobalt Schiff-base complex immobilized on magnetic iron oxide nanoparticles was prepared from commercially available and inexpensive substrates (Scheme 2).

The structure of cobalt complex supported on Fe_3O_4 as a heterogeneous catalyst was studied and characterized by Fourier transform infrared (FT-IR), X-ray powder diffraction (XRD), field -emission scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma (ICP) and vibrating sample magnetometry (VSM) analysis.

The prosperous synthesis of iron oxide nanoparticles was confirmed by the particular absorption peak of Fe—O bond at around 580 cm^{-1} and also, the band has seen at 3427 cm^{-1} can be related to the stretching vibrations of O—H band of the



Scheme 1. The synthesis of pyranopyrazole derivatives using cobalt complex immobilized on silica coated Fe_3O_4 magnetite nanoparticles.



Scheme 2. The sequence of events in the preparation of $Fe_3O_4@SiO_2@CoSB$.

nanoparticles surface (Fig. 1a). The peak at the range of 1000–1100 cm^{-1} verifies the silica modification on the nanoparticles (Fig. 1b). Fig. 1c displays the successful reaction between 3-chloropropyltrimethoxysilane and silica-coated Fe_3O_4 which is concluded by CH_2 stretching vibrations appearing at about 2927 cm^{-1} (asymmetric CH_2 stretch) and 2848 cm^{-1} (symmetric stretch). The band appeared at 1635 cm^{-1} exhibit the C=N stretching vibration band which pertains to attachment the Schiff-base complex on the modified nanoparticle [30].

Fig. 2 shows the XRD patterns of initial Fe_3O_4 and cobalt complex immobilized on silica coated Fe_3O_4 in the range of 10–80°. As represented in Fig. 2a, the XRD pattern exhibit diffraction lines of high crystalline nature at $2\theta = 18.5$, 30.5, 35.6, 43.7, 54, 57, 63 and 74.5. The XRD pattern of silica-coated magnetite nanoparticles (Fig. 2b) exhibited XRD broadened pattern because of its non-crystalline at $2\theta = 20$-30° which confirm $Fe_3O_4@SiO_2$ structure. The peak width (FWHM), size and interplanar distance from the XRD pattern of $Fe_3O_4@SiO_2@CoSB$ were investigated and the achieved results are summarized in Table 1. The crystallite size of the desired nanocatalyst was calculated to be (~10 nm) using Scherrer's equation, which was smaller than the size determined by field emission scanning electron microscopy analysis. The observed disagreement is dependent on the reality that XRD measurements investigate crystallite sizes of "coherently diffracting domains" of crystals while grains may contain several of these domains [51]. Also, the XRD pattern of cobalt complexes immobilized on Fe_3O_4 was same with neat Fe_3O_4, clearly indicating that crystallinity and morphology were not altered after grafting.

The morphology of nanocatalyst was studied by scanning electron microscopy (SEM). As can be seen, Fig. 3 indicated that most of the prepared nanoparticles are spherical shaped and have an average diameter of about 34 nm. The EDX spectrum of the attained $Fe_3O_4@SiO_2@CoSB$ as nanocatalyst exhibit, the presence of the anticipated elements in the structure of the catalyst, for iron (Fe), silicon (Si), oxygen (O), chlorine (Cl) and cobalt (Co) (Fig. 4).

Fig. 5 display the EDS-map of the elements in the structure of

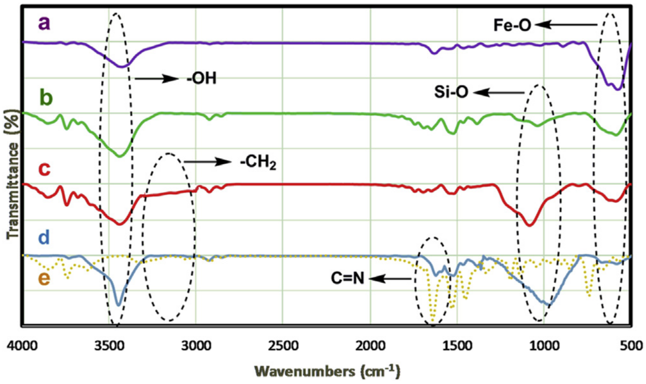


Fig. 1. FT-IR spectra of Fe_3O_4 (a), $Fe_3O_4@SiO_2$ (b), $Fe_3O_4@SiO_2@Cl$(c), $Fe_3O_4@SiO_2@CoSB$ (d) and neat cobalt Schiff-base (e).

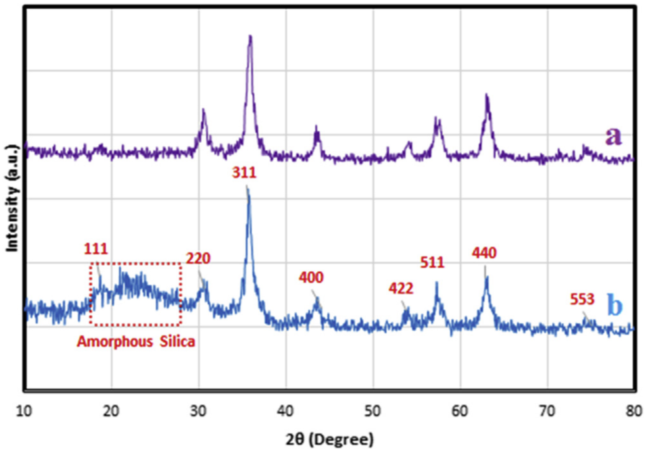


Fig. 2. XRD patterns of Fe_3O_4 (a) and $Fe_3O_4@SiO_2@CoSB$ (b).

Table 1
X-ray diffraction (XRD) data for the $Fe_3O_4@SiO_2@CoSB$ as a heterogeneous catalyst.

Entry	2θ	Peak width (FWHM) (°)	Size (nm)	Interplaner distance (nm)
1	18.6	1.24	6.47	0.466532
2	30.5	1.80	4.57	0.292741
3	35.8	1.00	8.35	0.250604
4	43.5	0.30	28.53	0.207795
5	54.0	1.80	4.95	0.169607
6	57.0	1.15	7.88	0.161371
7	63.0	1.05	8.88	0.147509
8	74.0	1.75	5.67	0.127949

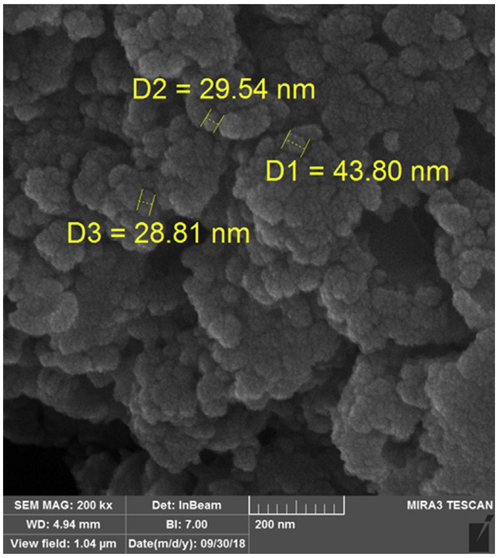


Fig. 3. SEM image of $Fe_3O_4@SiO_2@CoSB$

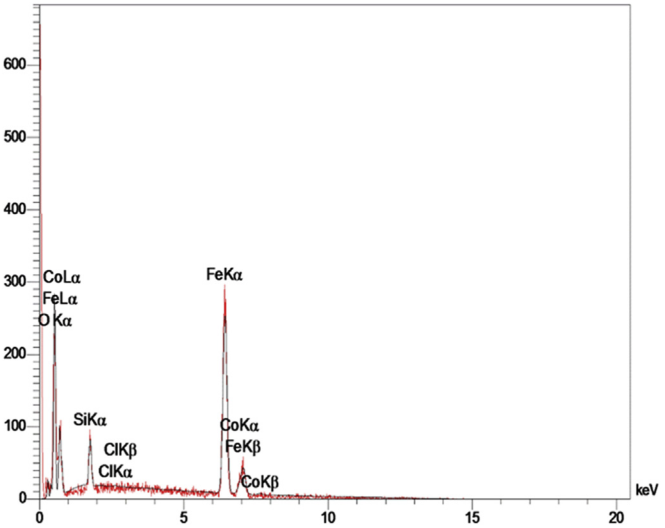


Fig. 4. EDS diagram of the Fe_3O_4@SiO_2@CoSB

nanocatalyst. According to the Figure, it can be concluded that the distribution of elements in the structure of the catalyst is monotonous and obviously this proves the stable connection of the catalyst into the complex. ICP analysis of the cobalt showed a value of about 0.315 mmol/g for Fe_3O_4@SiO_2@CoSB.

The magnetic properties of the nanocatalyst were studied using vibrating sample magnetometer (VSM) at room temperature. The magnetization curves measured for Fe_3O_4 and Fe_3O_4@SiO_2@CoSB are compared in Fig. 6. According to the magnetization curves, the saturation magnetization of the nanoparticles decreases from 53 emu g^{-1} for the initial Fe_3O_4 sample to 36 emu g^{-1} for nanocatalyst. According to the above results they are decreasing in saturation magnetization of the nanocatalyst compared to the bare nanoparticles relevant to the formation of silica shell and functionalized groups during the modification process. However, the catalyst still can be efficiently separated easily from the solution with the help of an external magnetic force.

Application of Fe_3O_4@SiO_2@CoSB as a heterogeneous catalyst in the synthesis of pyranopyrazole derivatives:

After successful preparation and characterization of Fe_3O_4@SiO_2@CoSB to find the best reaction conditions for the synthesis of pyranopyrazole derivatives, the reaction of 4-chloro benzaldehyde, malononitrile and 3- methyl-1-phenyl-2-pyrazoline-5-one with an equimolar ratio was initially examined as a model reaction. The effects of catalyst and temperature were investigated in the presence of various amounts of Fe_3O_4@SiO_2@CoSB (4–10 mg) at temperatures ranging from 25 to 100 °C (Table 2). In the absence of nanocatalyst, a low yield of the products was achieved after 60, and 40 min (Table 2, entries 1 and 2) and also a further increase in catalyst amount to 6 mg did not improve the product yield. According to the Table, the best results were obtained when the reaction was attained in the presence of 8 mg nanocatalyst at room temperature after 10 min (Table 2, entry 9).

The effect of different solvents on the catalytic activity of the Fe_3O_4@SiO_2@CoSB was investigated in the synthesis of pyranopyrazole derivatives (Table 3). Several solvents such as H_2O, ethanol, CH_3CN, CH_2Cl_2, Toluene, and *n*-Hexane were tested and the highest yield in the shortest reaction time was attained in the ethanol medium.

After optimization of the reaction conditions, to estimate the efficiency and scope of the nanocatalyst, we extended our study using Fe_3O_4@SiO_2@CoSB with different aromatic aldehydes to prepare a series of pyranopyrazoles (Table 4). A broad range of structurally various aromatic aldehydes (electron-donating substituents, electron-withdrawing substituents and halogens on their aromatic ring) were used in the facile reaction, giving very good to excellent yields. It is interesting to note that the yield of the reactions with aldehydes which having an electron-withdrawing

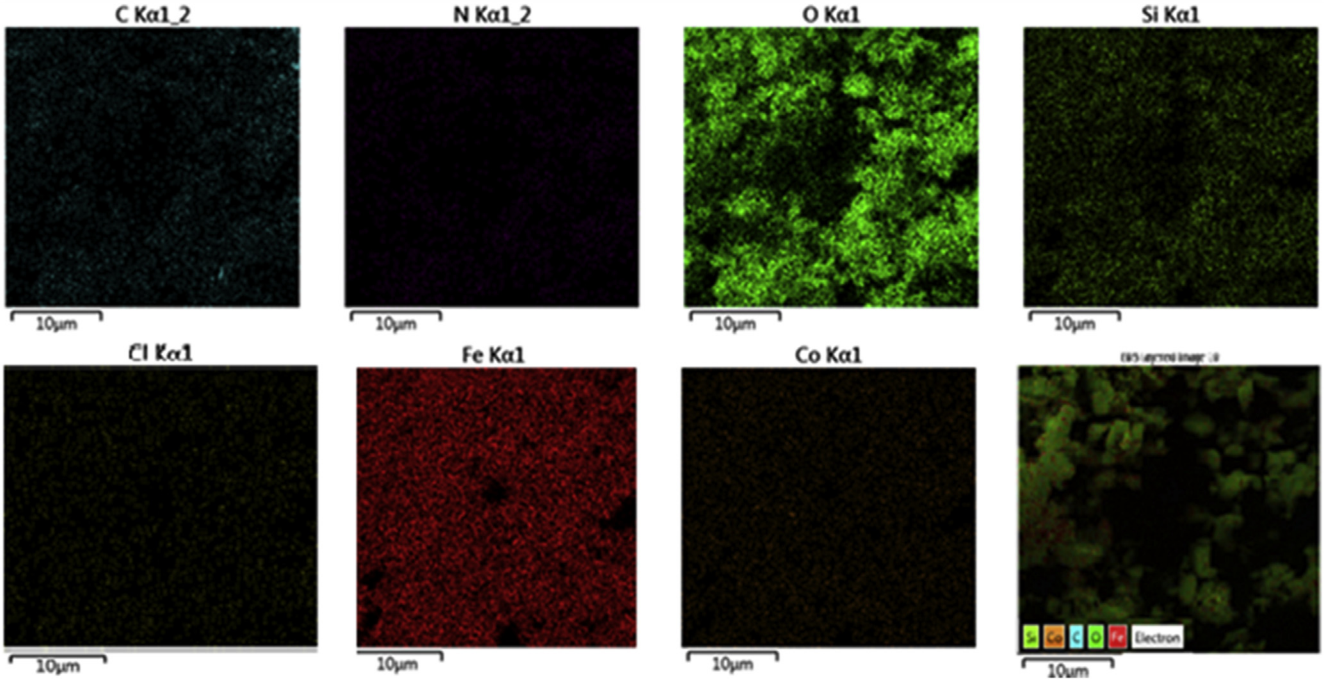


Fig. 5. EDS-MAP of the elements in the structure of Fe_3O_4@SiO_2@CoSB

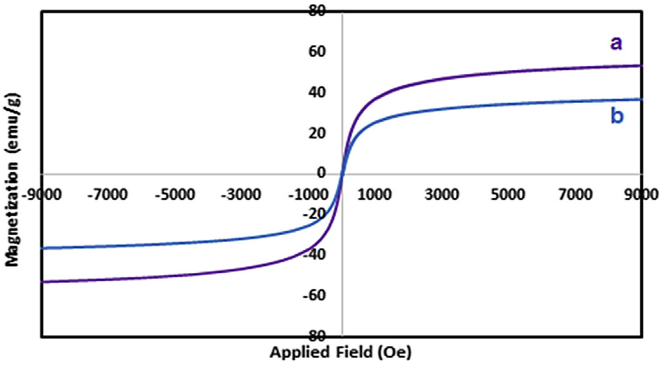
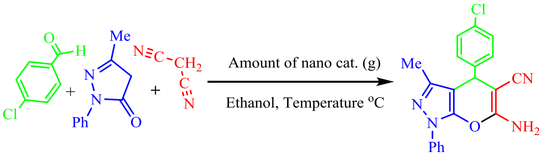


Fig. 6. The magnetic hysteresis loops of Fe_3O_4 MNPs (a) and $Fe_3O_4@SiO_2@CoSB$ (b).

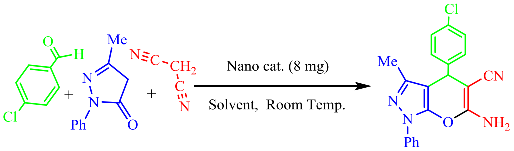
Table 2
The effect of catalyst amount and temperature on the three-component reaction of 4-chloro benzaldehyde, malononitrile and 3-methyl-1-phenyl-2- pyrazolin-5-one in ethanol as solvent. [a].



Entry	Amount of catalyst (mg)	Reaction temperature (°C)[b]	Reaction time (min)	Yield[c] (%)
1	–	r.t.	60	40
2	–	100	40	38
3	4	r.t.	30	60
4	4	100	30	65
5	6	r.t.	20	85
6	6	50	20	85
7	6	75	20	85
8	6	100	20	85
9	8	r.t.	10	95
10	8	50	10	95
11	8	75	10	95
12	8	100	10	95
13	10	r.t.	10	95
14	10	50	10	95
15	10	75	10	95
16	10	100	10	95

[a] Reaction conditions: 4-chloro benzaldehyde (1 mmol), malononitrile (1 mmol) and 3-methyl-1-phenyl-2- pyrazolin-5-one (1 mmol).
[b] This is the temperature of oil bath and not inside the reaction medium.
[c] I solated yield.

Table 3
The solvent effect in the reaction between 4-chloro benzaldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one[a] at room temperature using 8 mg catalyst..



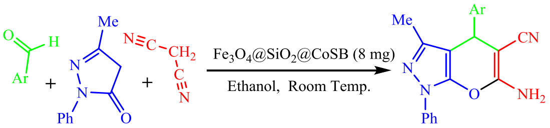
	Solvent-free	H_2O	C_2H_5OH	CH_3CN	CH_2Cl_2	Toluene	*n*-Hexane
Yield (%)[b]	80	70	95	60	40	40	45
Reaction time (min)	20	30	10	40	40	50	50

[a] Reaction conditions: 4-chloro benzaldehyde (1 mmol), malononitrile (1 mmol) and 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol) under room temperature.
[b] Isolated yield.

group was a little higher than that for those with an electron-releasing group (Table 4, entries 4, 6 and 8). Also it can be concluded that the location of the substituent in the derivatives are effective in the yield of the reaction. Furthermore, we calculated turn over numbers (TON) and turn over frequencies (TOF) states on the effectiveness of this nanocatalyst for the synthesis of all derivatives (Table 4). TON and TOF values for $Fe_3O_4@SiO_2@CoSB$ were calculated by the equations TON = Yield (%)/Catalyst amount (mol %) and TOF = Yield (%)/[Time (min) × Catalyst amount (mol%)] (according to the ICP results, 8 mg of nanocatalyst is equivalent to 0.252 mol% of catalyst) [52]. The results reveal that the nanocatalyst produces high TON and TOF values.

Furthermore, the additional probability to reuse and recycle the nanocatalyst for several runs was also studied. The results displayed in Fig. 7, approve that the magnetically separable nanocatalyst could be reused and recycled eight runs without any significant loss of activity and even after these runs, the yields remained still high. During the recycling experiment, no considerable change in the structure of the nanocatalyst was observed from XRD spectral studies for at least eight successive runs. This

Table 4
The three-component synthesis of pyranopyrazole derivatives in the presence of 8 mg of nanocatalyst..



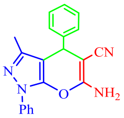
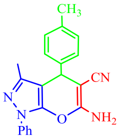
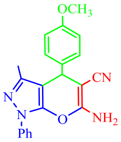
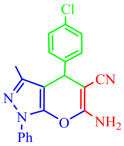
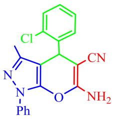
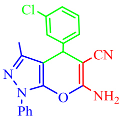
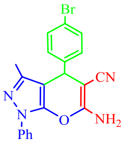
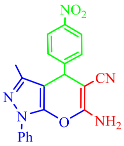
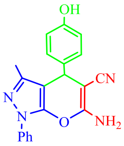
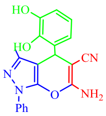
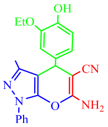
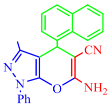
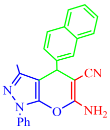
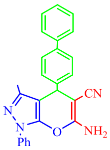
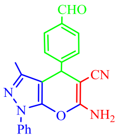
Entry	Product	Time (min)	Yield[b] (%)	TOF (min^{-1})[c]	TON[d]	M.p (°C) [Lit.]
1		10	91	36.11	361.11	170-172 [53]
2		25	88	13.96	349.20	180-182 [53]
3		30	85	11.24	337.30	177-179 [53]
4		10	95	37.69	376.98	170-172 [54]
5		15	92	24.33	365.07	150-152 [54]
6		15	94	24.86	373.01	161-163 [54]
7		15	93	24.60	367.58	180-182 [55]
8		10	98	38.88	388.88	200-202 [55]
9		30	85	11.24	337.30	195-197 [55]
10		25	85	13.49	337.30	165–167[e]

Table 4 (*continued*)

Entry	Product	Time (min)	Yield[b] (%)	TOF (min^{-1})[c]	TON[d]	M.p (°C) [Lit.]
11		25	84	13.33	333.33	174-176 [53]
12		15	90	23.80	357.14	234-236 [56]
13		15	92	24.32	365.07	214-216 [56]
14		20	90	17.85	357.14	187-189 [57]
15		15	92	24.32	365.07	227-228 [57]

[a]: Reaction conditions: different aldehydes (1 mmol), malononitrile (1 mmol) and 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), nanocatalyst (8 mg), ethanol as solvent and room temperature.

[b] Isolated yield.

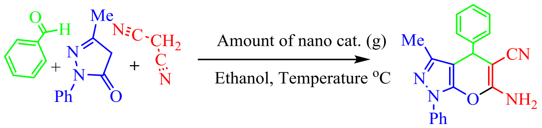
[c] Turnover numbers (TONs).

[d] Turnover frequencies (TOFs).

[e] New derivative.

Table 5

Comparison of the results of our studies with reported works..



Entry	Amount of catalyst	Solvent	Temp (°c)	Time (min)	Yield[b](%)	Ref.
1	Bovine serum albumin (60 mg)	H_2O–EtOH	r.t	90	94	[19]
2	[nano-Fe_3O_4@SiO_2@$(CH_2)_3$-Imidazole-SO_3H]Cl (7 mg)	Solvent free	r.t	30	91	[56]
3	TSA (10 mol%)	EtOH	reflux	10	95	[53]
4	FSM-16-SO_3H (40 mg)	EtOH/H_2O	reflux	40	88	[58]
5	Sulfamic acid (5 mol%)	EtOH	reflux	600	82	[59]
6	Fe_3O_4@SiO_2@CoSB (8 mg)	EtOH	r.t	10	91	This work

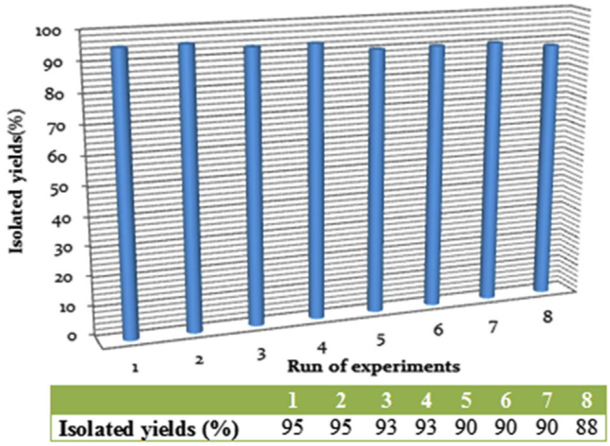
[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol) and 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol).

[b] Isolated yield.

data demonstrates the stability of the catalyst and perfect regeneration capacity of our nanocatalyst in mentioned reaction condition (Fig. 8).

A plausible mechanism for the synthesis of pyranopyrazole derivative (VII) in the presence of Fe_3O_4@SiO_2@CoSB is illustrated in Scheme 3. Initially, the aldehyde is activated using the cobalt Schiff-base complex moiety of nanocatalyst (I) to resulted (II). At that time, malononitrile (III) attacks to the carbonyl group of the activated aldehyde (II) and gives (IV) by the Knoevenagel condensation and loss of water molecule. The reaction is followed by the Michael addition of the methylene group of 3-Methyl-1-phenyl-2-pyrazolin-5-one (V) to an electron deficient carbon of dicyanoalkene (IV) to afford intermediate (VI), which converts to the pyranopyrazole (VII) via cyclization followed by tautomerization [53].

To compare the efficiency and scope of the nanocatalyst with some of those reported in the literature, a comparative result is presented in Table 5. In comparison with other catalysts employed for the synthesis of pyranopyrazole, our catalyst showed a much higher catalytic activity. According to these data, the yield of model reaction in the case of all the catalyst (except entries 1 and 3) is lower than Fe_3O_4@SiO_2@CoSB. Also, the comparison of the required



	1	2	3	4	5	6	7	8
Isolated yields (%)	95	95	93	93	90	90	90	88

Fig. 7. Reusability of Fe_3O_4@SiO_2@CoSB as a heterogeneous catalyst in 20 min.

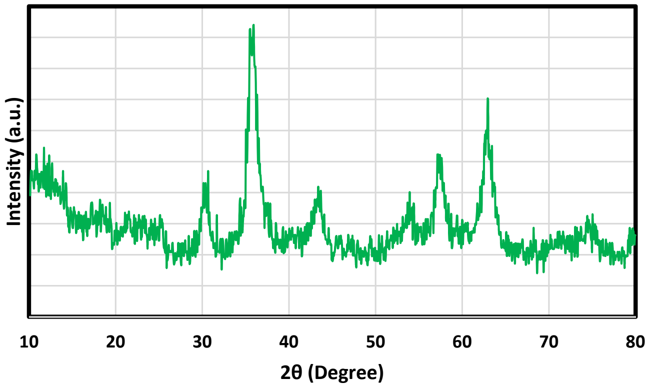
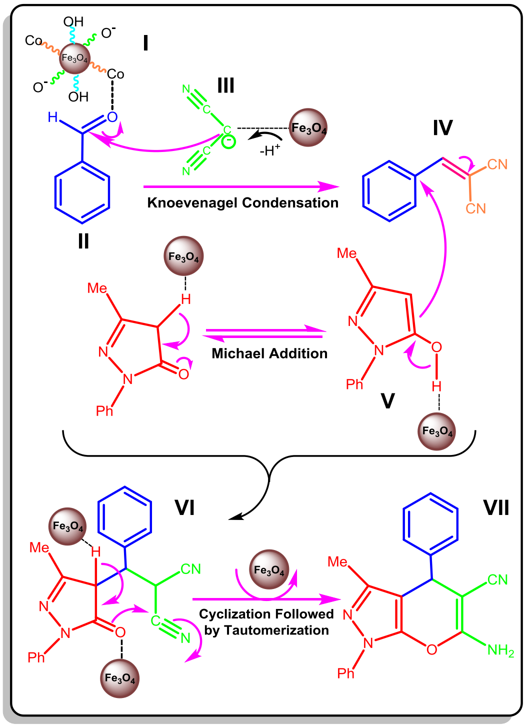


Fig. 8. Powder XRD pattern of reused Fe_3O_4@SiO_2@CoSB.



Scheme 3. The probable mechanism for the synthesis of pyranopyrazole derivatives using Fe_3O_4@SiO_2@CoSB as a nanocatalyst.

reaction time and temperature for those catalysts listed in the table with our catalyst indicate that the nanocatalyst synthesized here is convincingly superior to the recently reported catalytic methods. Additionally, it can be easily separated magnetically after the reaction and has shown great reusability.

4. Conclusion:

In summary, a new heterogeneous and reusable cobalt Schiff-base complex immobilized on magnetic Fe_3O_4 nanoparticles was designed and fully characterized by using different techniques. The catalytic applications of the described catalyst were investigated in the synthesis of pyranopyrazole derivatives under room temperature and ethanol as a green solvent. Notable advantages of this study are short reaction time, efficiency, the potential for recycling of the catalyst, high yield, easy experimental work-up, ease of handling of the catalyst with an external magnet.

Acknowledgements

We would like to thank the University of Tabriz, Tabriz, Iran to our research group for financial supports.

References

[1] H. Saeidian, M. Abdoli, R. Salimi, C. R. Chim. 16 (2013) 1063.
[2] M.C. Pirrung, K.D. Sarma, J. Am. Chem. Soc. 126 (2004) 444.
[3] A. Domling, Chem. Rev. 106 (2006) 17.
[4] S.L. Cui, X.F. Lin, Y.G. Wang, Org. Lett. 8 (2006) 517.
[5] A. Alizadeh, F. Movahedi, A.A. Esmaili, Tetrahedron Lett. 47 (2006) 4469.
[6] H.J. Wang, L.P. Mo, Z.H. Zhang, ACS Comb. Sci. 13 (2011) 181.
[7] A. Alizadeh, S. Rostamnia, L. Zhu, Tetrahedron Lett. 51 (2010) 4750.
[8] S. Rostamnia, E. Doustkhah, A. Nuri, J. Fluorine Chem. 153 (2013) 1.
[9] S. Rostamnia, K. Lamei, Synthesis 19 (2011) 3080.
[10] S. Rostamnia, A. Hassankhani, RSC Adv. 3 (2013) 18626.
[11] W.P. Smith, L.S. Sollis, D.P. Howes, C.P. Cherry, I.D. Starkey, N.K. Cobley, J. Med. Chem. 41 (1998) 787.
[12] J.L. Wang, D. Liu, Z.J. Zheng, S. Shan, X. Han, S.M. Srinivasula, C.M. Croce, E.S. Alnemri, Z. Huang, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 7124.
[13] M.E.A. Zaki, E.M. Morsy, M. Abdul, Heterocycl. Commun. 10 (2004) 97.
[14] N. Foloppe, L.M. Fisher, R. Howes, A. Potter, A.G.S. Robertson, A.E. Surgenor, Bioorg. Med. Chem. 14 (2006) 4792.
[15] H. Junek, H. Aigner, Chem. Ber. 106 (1973) 914.
[16] E. Safari, A. Hasaninejad, ChemistrySelect 3 (2018) 3529.
[17] T.N. Vasyun'kina, L.M. Bykova, V.N. Plotkin, S.M. Ramsh, Russ. J. Org. Chem. 41 (2005) 742.
[18] M. Babaie, H. Sheibani, Arab. J. Chem. 4 (2011) 159.
[19] K.S. Dalal, Y.A. Tayade, Y.B. Wagh, D.R. Trivedi, D.S. Dalal, B.L. Chaudhari, RSC Adv. 6 (2016) 14868.
[20] A. Siddekha, A. Nizam, M.A. Pasha, Spectrochem. Acta. A. 81 (2011) 431.
[21] S. Maddila, S. Rana, R. Pagadala, S. Kankala, S. Maddila, S.B. Jonnalagadda, Catal. Commun. 61 (2015) 26.
[22] J. Yu, H. Wang, Synth. Commun. 35 (2005) 3133.
[23] Y. Peng, G. Song, R. Dou, Green Chem. 8 (2006) 573.
[24] T.S. Jin, R.Q. Zhao, T.S. Li, Arkivoc Xiv, 2006, p. 176.
[25] M.M. Heravi, A. Ghods, F. Derikvand, K. Bakhtiari, F.F. Bamoharram, J. Iran. Chem. Soc. 7 (2010) 615.
[26] Z. Karimi-Jaberi, M.M. ReyazoShams, Heterocycl. Commun. 17 (2011) 177.
[27] Y.D. Zhao, D.W. Pang, Z. Zong, J.K. Cheng, Z.F. Luo, C.J. Feng, H.Y. Shen, X.C. Zhung, HuaxeXuebao 56 (1988) 178.
[28] A. Nishinaga, T. Yamada, H. Fujisawa, K. Ishizaki, J. Mol. Catal. 48 (1988) 249.
[29] S. Liu, J. Peng, H. Yang, Y. Bai, J. Li, G. Lai, Tetrahedron 68 (2012) 1371.
[30] J. Rakhtshah, S. Salehzadeh, E. Gowdini, F. Maleki, S. Baghery, M.A. Zolfigol, RSC Adv. 6 (2016) 104875.
[31] S. Rezaei, A. G-Choghamarani, R. Badri, Appl. Organomet. Chem. 30 (2016) 985.
[32] M. Kazemnejadi, A.R. Sardarian, RSC Adv. 6 (2016) 91999.
[33] A. Dewaele, F. Verpoort, B. Sels, ChemCatChem 8 (2016) 3010.
[34] S. Rostamnia, T. Rahmani, Appl. Organomet. Chem. 29 (2015) 471.
[35] A. Hajipour, Z. Shirdashtzade, G. Azizi, Appl. Organomet. Chem. 29 (2015) 143.
[36] A. Kamal, V. Srinivasulu, B.N. Seshadri, N. Markandeya, A. Alarifi, N. Shankaraiah, Green Chem. 14 (2012) 2513.
[37] M. Nasrollahzadeh, A. Azarian, A. Ehsani, M. Khalaj, J. Mol. Catal. A. 394 (2014) 205.
[38] Y.Z. Li, F.Y. Ma, X.T. Su, C. Sun, J.C. Liu, Z.Q. Sun, Y.L. Hou, Catal. Commun. 26 (2012) 231.
[39] C.R. Shen, S.T. Wu, Z.T. Tsai, J.J. Wang, T.C. Yen, J.S. Tsai, M.F. Shih, C.L. Liu,

Polym. Int. 60 (2011) 945.
[40] M. Heidarizadeh, E. Doustkhah, S. Rostamnia, P. Fathi Rezaei, F. Darvishi Harzevili, B. Zeynizadeh, Int. J. Biol. Macromol. 101 (2017) 696.
[41] S. Rostamnia, E. Doustkhah, J. Magn. Magn. Mater. 386 (2015) 111.
[42] M. Mohammadikish, M. Masteri-Farahani, S. Mahdavi, J. Magn. Magn. Mater. 354 (2014) 317.
[43] X. Li, Y. Fang, X. Zhou, J. Ma, R. Li, Mater. Chem. Phys. 156 (2015) 9.
[44] X. Cai, H. Wang, Q. Zhang, J. Tong, Z. Lei, J. Mol. Catal. A. 383−384 (2014) 217.
[45] S.A. Hamrahian, J. Rakhtshah, S.M. Mousavi Davijani, S. Salehzadeh, Appl. Organomet. Chem. 32 (2018), e4501.
[46] J. Rakhtshah, S. Salehzadeh, Res. Chem. Intermed. 43 (2017) 6973.
[47] J. Rakhtshah, S. Salehzadeh, M.A. Zolfigol, S. Baghery, Appl. Organomet. Chem. 31 (2017), e3690.
[48] J. Rakhtshah, S. Salehzadeh, M.A. Zolfigol, S. Baghery, J. Coord. Chem. 70 (2017) 340.
[49] M. Ma, Y. Zhang, W. Yu, H.Y. Shen, H.Q. Zhang, N. Gu, Colloids Surf., A 212 (2003) 219.
[50] W. Stober, A. Fink, E.J. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[51] H. Moghanian, A. Mobinikhaledi, A.G. Blackmanc, E. Sarough-Farahanib, RSC Adv. 4 (2014) 28176.
[52] M.A. Zolfigol, R. Ayazi-Nasrabadi, S. Baghery, RSC Adv. 5 (2015) 71942.
[53] M. Farahi, B. Karami, I. Sedighimehr, H.M. Tanuraghaj, Chin. Chem. Lett. 25 (2014) 1580.
[54] T.S. Jin, A.Q. Wang, Z.L. Cheng, J.S. Zhang, T.S. Li, Synth. Commun. 35 (2005) 137.
[55] A. Khazaei, M.A. Zolfigol, F. Karimitabar, I. Nikokar, A.R. Moosavi-Zare, RSC Adv. 87 (2015) 71402.
[56] M.A. Zolfigol, R. Ayazi-Nasrabadi, S. Baghery, V. Khakyzadeh, S. Azizian, J. Mol. Catal. A Chem. 418 (2016) 54.
[57] D. Azarifar, S.M. Khatami, M.A. Zolfigol, R. Nejat-Yami, J. Iran. Chem. Soc. 11 (2014) 1223.
[58] S. Hashemi-Uderji, M. Abdollahi-Alibeik, J. Iran. Chem. Soc. 15 (2018) 1.
[59] S.V. Shinde, W.N. Jadhav, J.M. Kondre, S.V. Gampawar, N.N. Karade, J. Chem. Res. 2008 (2008) 278.