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Preparation and characterization of ZrO₂-supported Fe₃O₄-MNPs as an effective and reusable superparamagnetic catalyst for the Friedländer synthesis of quinoline derivatives

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Abstract: In this study, a convenient, appropriate and eco-friendly method for the synthesis of quinoline derivatives *via* a Friedländer reaction was developed using ZrO₂/Fe₃O₄-MNPs as an effective and reusable heterogeneous catalyst. The morphology of ZrO₂/Fe₃O₄-MNPs was studied by the XRD, FT-IR, SEM, TEM and VSM techniques. Green reactions, straight and easy work-up, high yields of the products and good reaction times are the benefits of this procedure. Further, the catalyst could be recovered using an external magnetic field and reused at least three times without a considerable decrease in its catalytic activity.

Keywords: quinoline derivatives; Friedländer reaction; ZrO₂/Fe₃O₄-MNPs; heterogeneous catalyst; green procedure.

INTRODUCTION

Quinoline and its derivatives are very important intermediates in organic and medicinal chemistry that show various physiological and pharmacological activities, such as antimalarial, anti-inflammatory, anti-asthmatic, antibacterial, anti-hypertensive, and are tyrosine kinase inhibiting agents.^{1–3} These heterocycles are valuable compounds for the preparation of nano- and meso-structures with enhanced electronic and photonic properties.^{4,5} Furthermore, quinoline derivatives have been employed in the study of bio-organic and bio-organometallic processes.^{6,7} Due to the importance of the use of quinolines in the fields of medicinal, bioorganic, industrial and synthetic organic chemistry, there is immense interest in the development of effective procedures for their synthesis. Thus, several methods, such as the Skraup, Doebner–von Miller, Friedländer and

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Combes, have been mentioned in the literature for the creation of quinoline derivatives.^{8–11}

Among various methodologies suggested for the preparation of quinolines, the Friedländer annulation^{12,13} is one of the most frequently used pathways for the synthesis of polysubstituted quinolines. This method involves an acid- or base-catalyzed or thermal condensation between an aromatic 2-aminoaldehyde or ketone with a carbonyl compounds containing a reactive α -methylene group followed by a cyclodehydration.^{14,15}

In general, Friedländer reactions are carried out either by refluxing an aqueous or alcoholic solution of reactants in the presence of a base or by heating a mixture of the reactants at high temperatures ranging from 150 to 220 °C in the absence of a catalyst.¹⁶ However, under thermal or basic catalysis conditions, 2-aminobenzophenone does not react with simple ketones, such as cyclohexanone and β -keto esters.¹⁷ Subsequent work showed better yields of quinolines were achieved under acid catalysis.¹⁷ Several acid catalysts, such as Brønsted acids including hydrochloric acid in water,¹⁸ sulfamic acid,¹⁹ sulfuric acid,²⁰ silica sulfuric acid,²¹ dodecylphosphonic acid,²² PEG-supported sulfonic acid,²³ arylidene pyruvic acids (APAs),²⁴ oxalic acid,²⁵ Lewis acids containing $Zr(NO_3)_4$ or $Zr(HSO_4)_4$,²⁶ zirconium tetrakis(dodecyl sulfate) $Zr(DS)_4$,²⁷ $GdCl_3 \cdot 6H_2O$,²⁸ $BiCl_3$,²⁹ $SnCl_2$,³⁰ $FeCl_3$,³¹ $Y(OTf)_3$,³² $NiCl_2$,³³ $Ag_3PW_{12}O_{40}$ ³⁴ and $ZnCl_2$ ³⁵ have been reported for this conversion.

However, most of the previously reported procedures suffer from different drawbacks, such as low yields of the products, poor selectivity, long reaction times, harsh conditions, high temperatures, usage of hazardous, corrosive and relatively expensive catalysts, tedious work-up procedures and using toxic/polar solvent leading to complex isolation and recovery procedures. Moreover, the main disadvantage of a number of previous methods is that the catalyst cannot be recovered. Therefore, the development of a simple, efficient and environmentally friendly method for the synthesis of quinoline derivatives is still a challenging task.

Recently, the applications of heterogeneous nanocatalysts have attracted remarkable attention as inexpensive, non-toxic and eco-friendly catalysts for various organic transformations under mild and convenient conditions. The catalysts have advantages over conventional homogeneous catalysts, including simple recovery from the reaction mixture by easy filtration, higher surface activity and reusability.^{36–38}

Among heterogeneous catalysts, inorganic oxides especially zirconia have different physical and chemical properties and have gained much consideration by researchers. Good chemical and dimensional stability, high electrical resistivity, high refractive index, mechanical strength and toughness, biocompatibility and low cost are the origin of the interest in using the zirconia as a catalyst.^{39,40}

However, the specific surface area and thermal stability of pure ZrO₂ is low⁴¹ and it shows weak catalytic activity in a number of chemical transformations.⁴²

In order to enhance the catalytic performance of zirconia-based catalysts, many endeavors have been inducted by introducing various metal oxides whereupon zirconia acts as a support for the preparation of the solid catalysts.^{43–48} Although the doping of appropriate cations with specific concentration into zirconia improves thermal stability, surface area and acidity of solid acids, the separation and recovery of mixed oxide catalysts from the reaction products are still difficult and require a large amount of separation energy and cost. For this reason, a material immobilized onto the solid support plays a fundamental role in the efficiency of the resulting supported reagent catalyst. Among the different modified zirconia materials, Fe₃O₄ magnetic nanoparticles (MNPs) are widely used due to easy handling, a simple work-up procedure, nontoxicity, enhanced catalytic activity and chemical selectivity in various organic synthesis.^{49,50} In addition, ZrO₂-supported Fe₃O₄-MNPs can be easily separated from the reaction media by applying an external magnetic field.

In continuation of ongoing studies on metal oxides as catalysts,⁵¹ herein, a simple and eco-friendly procedure is demonstrated for the synthesis of quinoline derivatives using the Friedländer heteroannulation method in the presence of ZrO₂/Fe₃O₄-MNPs as catalyst.

EXPERIMENTAL

Chemicals and apparatus

All materials and solvents were purchased from Merck and Fluka, and used without further purification. Yields refer to isolated products. Products were characterized by their physical constants, comparison with authentic samples, and IR and NMR spectroscopy. The IR spectra were obtained in KBr discs on a Perkin–Elmer model Spectrum One FT-IR spectrometer.

The structures of the synthesized catalysts were characterized by X-ray diffraction analysis (XRD Equinox 3000, INEL, France). The XRD patterns were obtained using CuK_α radiation (wavelength 1.54056 Å) at a current of 200 mA and a voltage of 40 kV in the 2θ range of 10–100 at a scanning rate of 8° min⁻¹. The surface microscopic morphologies of the ZrO₂-supported Fe₃O₄-MNPs were visualized by scanning electron microscopy (SEM MIRAI TESCAN). The size of Fe₃O₄-MNPs was investigated by transmission electron microscopy (TEM Philips MC 10) with an acceleration voltage of 80 kV. A magnetic study was performed using a vibrating sample magnetometer at room temperature (VSM JDM-13).

Reaction progress was checked by thin-layer chromatography (TLC) with detection by UV light. The ¹H-NMR spectra were obtained on a Bruker DRX-400 Avance spectrometer, while the ¹³C-NMR spectra were obtained on a Bruker DRX-100 Avance spectrometer. Samples were analyzed in CDCl₃ and chemical shift values are reported in ppm relative to tetramethylsilane (TMS) as the internal reference. Melting points were measured on an electrothermal apparatus and are uncorrected. Elemental analyses were realized using a Carlo Erba EA1110 CHNS-O analyzer and the values agreed with the calculated ones.

Preparation of the catalyst (ZrO₂/Fe₃O₄-MNPs)

Firstly, 96 mg of ZrO₂ nano particles were well dispersed in 30 mL of distilled water in a two-necked round bottom flask (100 mL) by ultrasonic irradiation for 30 min. After adding 81 mg of FeCl₃·6H₂O, the solution was stirred vigorously for 30 min. Subsequently, 120 mg FeCl₂·4H₂O was slowly added into the mixture under stirring for 30 min. The whole process was performed under an argon atmosphere. Then, 8 mL of a concentrated aqueous solution of NH₃ was added into the solution dropwise over 1 h. Thereafter, the mixture was stirred at 60 °C for 2 h. After cooling the solution to room temperature, the black magnetic ZrO₂/Fe₃O₄-MNPs were recovered by centrifugation at 6000 rpm, rinsed several times with deionized water and dried at 60 °C for 24 h. It was expected that the positive ferrous and ferric ions would be in proximity with the oxygen atoms of ZrO₂ and that they would be converted to Fe₃O₄-MNPs after the dropwise addition of the concentrated aqueous solution of NH₃ into the solution.

General procedure for the synthesis of quinolines catalyzed by ZrO₂/Fe₃O₄-MNPs

A mixture of 2-amino-5-chlorobenzophenone (1 mmol), a ketone or β -diketone (1.5 mmol) and ZrO₂/Fe₃O₄-MNPs (20 mg) in ethanol (5 mL) was stirred magnetically and heated at 70 °C. After completion of the reaction, confirmed by TLC, the catalyst was collected by magnetic separation using an external magnet and washed repeatedly with warm ethanol. The aqueous phase was filtrated and cooled to room temperature. Then the solid product was collected and washed with cold water to afford the pure product. In some cases, further purification was achieved by recrystallization in ethanol to give the pure product.

RESULT AND DISCUSSION

Catalyst characterization

X-Ray diffraction studies. To confirm the synthesis of the catalyst, first, the XRD patterns of the pure ZrO₂ nanoparticles and ZrO₂/Fe₃O₄ magnetic nanoparticles were studied. All the diffraction peaks in the XRD patterns of the pure ZrO₂ imply the monoclinic phase of pure ZrO₂ nanoparticles (*m*-ZrO₂, JCPDS NO 24-1165). The additional diffraction peaks at 2θ 30.6, 36.5, 43.7, 53.9, 57.6, and 62.8° appearing in the XRD patterns of the ZrO₂/Fe₃O₄-MNPs correspond to the standard XRD data for the cubic Fe₃O₄ phase of inverse spinel crystal structure (JCPDS file No. 19-0629).⁵² No peaks corresponding to impurities were present. The average diameter of the crystallites (*D*) of the synthesized catalyst was calculated using the Scherrer formula and found to be 21 nm, as confirmed by TEM analysis.

Fourier transform infrared spectroscopy. The FT-IR spectrum of pure zirconia was compared with the synthesized ZrO₂/Fe₃O₄-MNPs. The pure zirconia spectrum exhibited bands at 734, 581 and 508 cm⁻¹, which could be attributed to the Zr–O stretching vibration of ZrO₂. These bands were not distinctly found in the spectrum of ZrO₂/Fe₃O₄-MNPs. They are related to the broad band at around 579 cm⁻¹, which was assigned to the Fe–O stretching vibration of Fe₃O₄-MNPs that may overlap with the Zr–O peaks. Moreover, the absorption bands in the

region 3435 and 1630 cm^{-1} may be related to the stretching and bending vibrations of the O–H bond due to physically adsorbed water molecules.

SEM and TEM analysis. The morphology and size of the synthesized $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ -MNPs were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM image (Fig. 1a), it can be seen that the loaded Fe_3O_4 -MNPs were uniform in shape and size distribution and had a porous structure. The particles sizes derived from TEM analysis (Fig. 1b) were in the range $5\text{--}25\text{ nm}$, which is comparable with the crystallite size calculated from the X-ray spectrum.

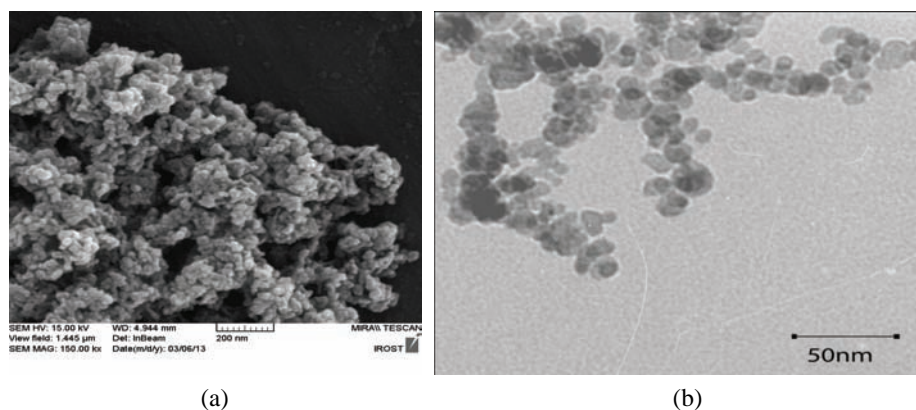


Fig. 1. a) SEM and b) TEM image of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ -MNPs.

Vibrating sample magnetometer (VSM) analysis

The magnetic properties of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ magnetic nanoparticles were investigated by the most common method of examining the magnetic properties of a material, using a vibrating sample magnetometer (VSM). The results showed that the synthesized nanoparticles exhibit superparamagnetic behavior at room temperature and the hysteresis loops of the samples exhibited no coercivity and retentivity. The saturation magnetization (M_s) values of the synthesized catalysts were 33 emu g^{-1} , which is mainly attributed to a high weight ratio of Fe_3O_4 magnetic nanoparticles that were loaded onto the ZrO_2 .

Catalyst synthesis optimization

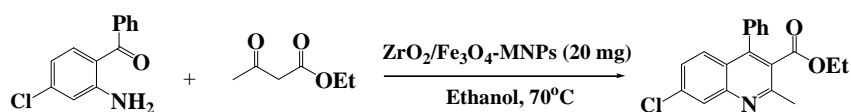
At the beginning of the investigations on the usage of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ -MNPs as a green and efficient heterogeneous nanocatalyst, the reaction of 2-amino-5-chlorobenzophenone and ethyl acetoacetate (EAA) was selected as a model for determining the optimal conditions. For this reason, several reactions were performed using diverse amounts of catalyst at various temperatures in different solvents to achieve a good yield of the desired products. The results are summarized in Table I.

TABLE I. Optimization of the conditions for the synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate; reaction conditions: 2-amino-5-chlorobenzophenone (1 mmol), EAA (1.5 mmol) in different solvents at different temperatures with different amount of catalyst

Entry	Catalyst [amount, mg]	Solvent	<i>t</i> / °C	τ / min	Yield ^a , %
1	–	Ethanol	Reflux	300	Trace
2	ZrO ₂ -NPs [300]	Ethanol	Reflux	240	18
3	ZrO ₂ /Fe ₃ O ₄ -MNPs [10]	Ethanol	Reflux	60	88
4	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Ethanol	Reflux	24	91
5	ZrO ₂ /Fe ₃ O ₄ -MNPs [30]	Ethanol	Reflux	25	90
6	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Ethanol	25	320	Trace
7	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Ethanol	50	300	51
8	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Ethanol	70	25	92
9	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Methanol	Reflux	30	86
10	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	Acetonitrile	70	120	22
11	ZrO ₂ /Fe ₃ O ₄ -MNPs [20]	<i>n</i> -Hexane	Reflux	120	Trace

^aIsolated yield

As can be seen in Table I, the best result was obtained when the reaction was performed at 70 °C, with a relative ratio of the substrate: EAA:ZrO₂/Fe₃O₄-MNPs of 1 mmol:1.5 mmol:20 mg, respectively (Table I, entry 8). In this procedure, any further increase in temperature and amount of catalyst did not lead to considerable improvement in the reaction times and yields. Moreover, when the same procedure was run at room temperature, the yield of the product was poor after 320 min (Table I, entry 6). It is noteworthy that without any catalyst at reflux, the product was isolated in low yield after a long reaction time (Table I, entry 1). Moreover, it can be seen that the pure *m*-zirconia as the catalyst led to a lower yield of the product (Table I, entry 2). In order to examine the effect of the solvent, the reaction was explored in different solvents, *i.e.*, ethanol, methanol, acetonitrile and *n*-hexane (Table I, entries 8–11) and ethanol was selected as the best solvent. Under the optimized conditions, the model reaction gave 92 % yield of the corresponding product after 25 min (Table I, entry 8 and Scheme 1).



Scheme 1. ZrO₂/Fe₃O₄-MNPs catalyzed synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate.

Subsequently, in order to evaluate the generality of this methodology, a series of *ortho*-aminoaryl ketones were reacted with different 1,3-dicarbonyl compounds under the optimum conditions and the results are reported in Table II.

TABLE II. Synthesis of various quinolines using ZrO₂/Fe₃O₄-MNPs as the catalyst; reaction condition: 2-aminoaryl ketone (1 mmol), ketone or β-diketone (1.5 mmol) and ZrO₂/Fe₃O₄-MNPs (20 mg) at 70 °C in ethanol (5 mL)



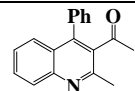

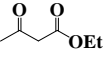
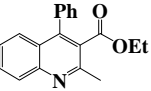

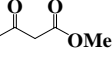
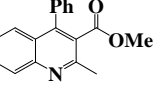

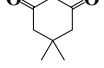
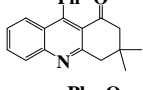

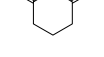
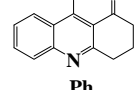


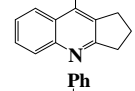


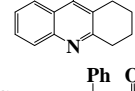
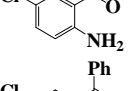

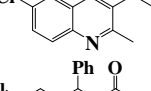
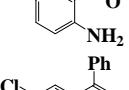
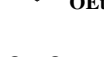
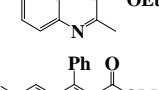
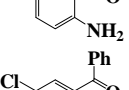
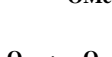
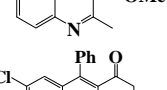
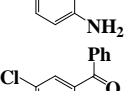
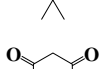
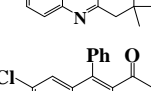
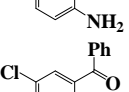

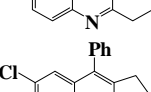
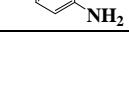

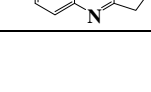
Entry	Substrate	Ketone or β-diketone	Quinoline	τ min	Yield ^a %	M.p., °C	
						Measured	Reported
1				40	89	109–111	111–112 ²⁵
2				30	91	98–100	100–101 ²⁵
3				35	90	99–100	98–100 ⁵³
4				60	86	191–194	190–192 ³⁴
5				45	90	154–156	155–156 ³⁴
6				50	89	129–131	130–132 ³⁴
7				60	87	153–156	156–157 ³⁴
8				45	90	151–153	150–151 ³⁴
9				25	92	101–103	102–104 ²²
10				30	90	134–136	133–135 ²⁵
11				45	89	207–209	208–209 ³⁴
12				35	92	184–186	185–186 ³⁴
13				45	90	107–108	106–107 ²⁵

TABLE II. Continued

Entry	Substrate	Ketone or β -diketone	Quinoline	τ min	Yield ^a %	m.p., °C	
						Measured	Reported
14				60	89	165–167	164–165 ³⁴
15				65	87	239–241	240–243 ⁵⁴

^aIsolated yield

According to Table II, both cyclic and acyclic diketones such as 5,5-dimethylcyclohexanedione and acetylacetone, cyclic ketones including cyclohexanone and cyclopentanone and β -ketoesters such as EAA reacted with 2-amino-5-chlorobenzophenone and 2-aminobenzophenone to afford the corresponding quinolines. It can easily be seen that in all cases, the Friedländer annulation proceeded smoothly and gave good to high yields ranging from 86 to 92 %. The reactions were remarkably clean and no chromatographic separation was necessary to obtain spectra-pure compounds. Furthermore, the work-up of present method was easy and the process is beneficial in avoiding the application of strong acids, high temperatures and volatile and/or toxic reactants. All of the synthesized products are known compounds and were characterized by comparing their melting points, IR, ¹H- and ¹³C-NMR spectra with those of authentic samples.

The possibility of reusing the catalyst is one of the most significant benefits of heterogeneous catalysts over homogeneous systems. Thus, the recovery and reusability of ZrO₂/Fe₃O₄-MNPs was investigated in the model reaction under the optimized condition. After completion of the reaction, the catalyst was easily separated from the reaction mixture by an external magnetic field and reused in subsequent runs. The results of continuous runs showed that the recovered catalyst could be reused three times without any appreciable decrease in its activity (Table III). The strength of catalyst is emphasized *via* measurement of Fe ions leaching by atomic absorption spectroscopy and trace metal ions were detected in the filtrate of this reaction.

TABLE III. Reusability of the ZrO₂/Fe₃O₄-MNPs in the model reaction (Table II, entry 8)

Run No.	τ / min	Yield, %
1	25	92
2	25	92
3	27	90
4	30	88

Moreover, in order to demonstrate the excellent catalytic activity of ZrO₂/Fe₃O₄-MNPs and the performance of this method, some of the results obtained

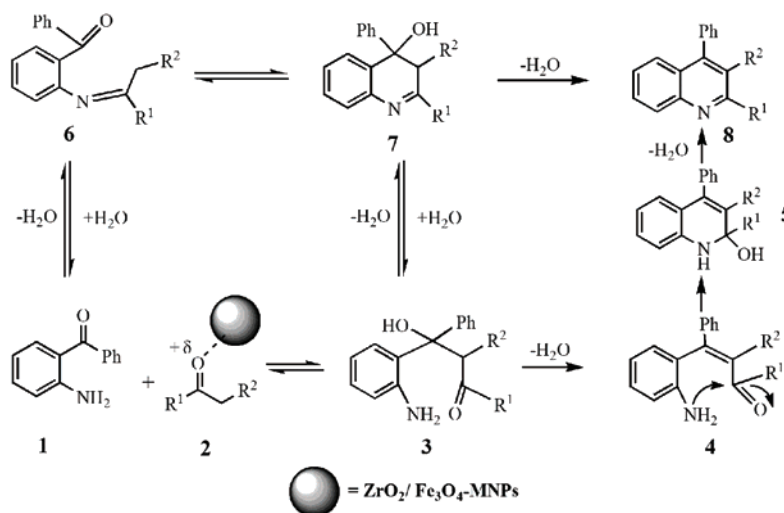
by the presented procedure were compared with other previously reported heterogeneous catalytic systems in the literature. As shown in Table IV, the obtained results show the advantage of the present protocol in terms of catalyst amount, yields or reaction times.

TABLE IV. Comparison of the result obtained for the synthesis of model reaction (Table II, entry 8) using ZrO₂/Fe₃O₄-MNPs with other catalysts reported in the literature

Entry	Catalyst amount	Solvent	<i>t</i> / °C	τ / min	Yield ^a , %	Reference
1	(BSPY)HSO ₄ /MCM-41 (70 mg)	–	100	80	94	55
2	NH ₂ SO ₃ H (5 mol %)	–	70	45	89	56
3	SiO ₂ /I ₂ (100 mg/50 mg)	–	60	120	80	57
4	Amberlyst-15 (10 % w/w)	C ₂ H ₅ OH	Reflux	150	87	58
5	Nano-Flake ZnO (10 mol %)	–	100	120	92	59
6	ZrO ₂ /Fe ₃ O ₄ -MNPs (20 mg)	C ₂ H ₅ OH	70	25	92	This Work

^aIsolated yield

Two possible mechanisms exist for the Friedländer synthesis of quinolines that are shown in Scheme 2. Based on these mechanisms and in the first step, the carbonyl group is activated by ZrO₂/Fe₃O₄-MNPs. Then, 2-amino-5-chloro substituted carbonyl compound **1** and carbonyl compound **2** react in a rate-limiting step to the aldol adduct **3**. This intermediate loses water in an elimination reaction to the unsaturated carbonyl compound **4** and then loses water again in imine formation to quinoline **5**. In the second mechanism, the first step is Schiff base formation to **6** followed by an aldol reaction to **7** and elimination to **8**.



Scheme 2. Proposed mechanism for the synthesis of quinoline derivatives in the presence of ZrO₂/Fe₃O₄-MNPs.

CONCLUSIONS

In conclusion, a green, one-pot, effective and environmentally friendly approach has been explained for the synthesis of quinoline derivatives *via* Friedländer annulation using ZrO_2/Fe_3O_4 -MNPs as a convenient, mild and reusable catalyst. The remarkable benefit of the described method include good substrate generality, mild reaction conditions, high yields, good reaction times, simple experimental procedure, the use of a low cost catalyst, easy work-up, clean reaction profiles and green conditions by avoiding the usage of toxic organic solvents. Furthermore, the catalyst was successfully recovered and reused at least for four runs without significant loss in its activity, which make the presented procedure an interesting alternative to previously reported methods.

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ИЗВОД

ДОБИЈАЊЕ И КАРАКТЕРИЗАЦИЈА ZrO_2/Fe_3O_4 МАГНЕТНИХ НАНОЧЕСТИЦА (MNPs) КАО ЕФИКАСНОГ СУПЕРПАРАМАГНЕТНОГ КАТАЛИЗАТОРА ЗА ФРИДЛЕНДЕРОВУ СИНТЕЗУ ДЕРИВАТА ХИНОЛИНА

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Током истраживања развијен је приступачан и еколошки прихватљив поступак синтезе деривата хинолина Фридлендеровом реакцијом, употребом ZrO_2/Fe_3O_4 -MNPs као ефикасног хетерогеног катализатора. Морфологија ZrO_2/Fe_3O_4 -MNPs је испитана XRD, FT-IR, SEM, TEM и VSM аналитичким техникама. Предности овог поступка су лака обрада реакционе смеше, висок принос производа и кратко реакционо време. Употребљен катализатор се уклања спољашњим магнетним пољем и може се поново употребити најмање три пута без значајнијег смањивања каталитичке активности. Током синтезе и обраде реакционе смеше избегава се употреба органских растварача што целокупан процес чини еколошки прихватљивим.

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