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Synthesis, characterization and heterogeneous catalytic application of an immobilized nickel(II) Schiff-base complex supported on MWCNTs for the Hantzsch four-component condensation

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Immobilized nickel(II) Schiff-base complex supported on multi-wall carbon nanotubes (MWCNTs) as a highly efficient heterogeneous catalyst was synthesized and characterized by IR, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma (ICP), elemental analysis (CHN) and thermal gravimetric analysis (TGA). Then a facile and environmentally benign procedure was developed for synthesis of polyhydroquinoline derivatives *via* Hantzsch one-pot condensation reaction of aromatic aldehydes, 1,3-diones, ethyl acetoacetate and ammonium acetate in the presence of an immobilized nickel(II) Schiff-base complex supported on MWCNTs as a reusable heterogeneous catalyst under solvent-free conditions. This protocol has the advantages of stability, easy availability, recyclability and eco-friendly catalyst, simple experimental, high to excellent yields and work-up procedure. Considering the solvent free condition and also temperature, time and yield of the model reaction the nano-catalyst reported here is among the best catalysts reported so far for synthesis of polyhydroquinolines.

Keywords: Immobilized Ni(II)-Schiff base complex supported on MWCNTs; Polyhydroquinolines; Hantzsch condensation; Solvent-free

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1. Introduction

Schiff bases can be easily synthesized and form complexes with almost all metal ions. Many Schiff base complexes demonstrate excellent catalytic activity in various reactions at high temperature (up to 100 °C) and in the presence of moisture [1]. Schiff bases stabilize many different metals in various oxidation states, controlling the performance of metals in a wide range of practical catalytic transformations [2]. Over the past few years, there have been many reports on their applications as catalyst in reactions such as polymerization reaction [1], reduction [3], oxidation of organic compounds [4], hydrosilylation of ketones [5], synthesis of bis(indolyl) methanes [6] and Diels–Alder reactions [7]. Specifically, Schiff base complexes of nickel(II) and copper(II) have increased enantioselectivity in alkylation of enolates [8],

Due to unusual properties of multi-wall carbon nanotubes (MWCNTs) such as structural and thermal stability and also insolubility in the most solvents, they are promising supports for immobilizing catalytic species and have considerable benefits [9-14]. Metal complexation has been a recent choice for functionalization of CNTs and fabrication of CNTs/inorganic hybrid materials. Although a few examples have been established for complexation, this field has not been fully investigated [15]. However, some efforts have been made to immobilize nickel complexes on the surface of various supports. For example, a paper by Salavati and co-workers introduces the immobilization of a Ni(II)-salen complex on MWCNTs and reports the resulting heterogeneous catalysts for oxidation of phenol with hydrogen peroxide [12]. Khatri and Farahani reported a rhenium-oxo complex such as methyltrioxorhenium (MTO) immobilized on modified graphene oxide (GrO) and also a molybdenum–Schiff base complex supported on MWCNTs via covalent bonding [16, 17].

We report here the synthesis and characterization of a nickel(II) Schiff base complex, which is covalently attached to the MWCNTs, and its application on the green, sequential, one-pot four-component protocol for synthesis of polyhydroquinoline derivatives via the Hantzsch reaction between aromatic aldehydes with 1,3-diones, ethyl acetoacetate and ammonium acetate under solvent-free conditions at room temperature (scheme 1).

150 years after the first multi-component reaction (MCR), there is still an ongoing and widespread interest in this field, having been re-invigorated with the development of high-speed synthesis and the necessity for new highly flexible chemical starting points in drug discovery. Increase of MCRs has broadly resulted in the rapid assembly of arrays with high-molecular

diversity [18, 19]. In 1882, Arthur Hantzsch described first synthesis of symmetrically substituted 1,4-dihydropyridine derivatives via the one-pot, four component condensation of two molecules of ethylacetoacetate, aromatic aldehyde and ammonia [20]. Polyhydroquinoline derivatives are an important group of nitrogen heterocycles of importance because of their different therapeutic and pharmacological properties, antitumor, vasodilator, calcium channel blockers, bronchodilator, anti-atherosclerotic, geroprotective, hepatoprotective and antidiabetic activity [21-25]. Various methods have been described for the synthesis of polyhydroquinoline derivatives, due to the biological significance of these compounds. The classical method includes three-component coupling of an aldehyde with ethyl acetoacetate and ammonia in acetic acid or in refluxing alcohol [26-30]. These methods suffer from disadvantages such as lower yields, an excess of organic solvent, a long reaction time and harsh refluxing conditions. Therefore, chemists have developed more efficient methods for synthesis of polyhydroquinoline derivatives, which involve the use of microwave irradiation [31], solar thermal energy [32], solvent-free conditions on grinding [33], refluxing at high temperature [34], and using various catalysts such as bismuth(III) bromide [35], L-proline [36], {[HMIM]C(NO₂)₃} [37], K₇[PW₁₁CoO₄₀] [38], HY-zeolite [39], [pyridine-SO₃H]Cl [40], nanoparticles [41], ceric ammonium nitrate [42], [2-MPyH]OTf [43], boronic acids [44], Cu(II) and Mn(III) Schiff base complex [45], HClO₄-SiO₂ [46], Baker's yeast [47], polymers [48], PTSA-SDS [49], and iodine [50].

Nanoscale heterogeneous catalysts propose higher surface area and low-coordinate metal sites, which are responsible for higher catalytic activity. Furthermore, heterogeneous catalysis has the advantage of easy product purification, high atom-efficiency and reusability of the catalyst [51, 52].

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Scheme 1. Hantzsch four-component condensation using immobilized nickel(II) Schiff-base complex supported on MWCNTs.

2. Experimental

2.1. Materials and instrumentation

All chemicals were attained from Merck, Fluka and Sigma Aldrich chemical companies. Multiwalled carbon nanotubes of >85% purity and length 1-10 mm, outer diameter, 5–20 nm were purchased from Kermanshah petrochemical industries company. The identified compounds were analyzed by comparison of their physical properties and spectral data with reliable samples in the literature. Reaction progress and purity determination of the compounds were tested *via* TLC using silica gel SIL G/UV 254 plates. The ¹H NMR (250) and ¹³C NMR (62 MHz) spectra were recorded on a Bruker spectrometer (δ in ppm). Melting points are uncorrected and were recorded on a Buchi B-545 apparatus in open capillary tubes.

2.2. *Immobilized nickel(II) Schiff-base complex supported on MWCNTs, preparation and purification*

The raw MWCNTs were first immersed in an aqueous solution of HF to remove SiO₂, then filtered and washed with deionized water and THF and dried in an oven. Following careful

purification, MWCNTs were oxidized in a mixture of concentrated sulfuric and nitric acids (3:1, 98 and 70%, respectively) by ultrasonication for 24 h to obtain MWCNT-COOH [53]. In order to increase the reactivity and/or population of OH surface groups, the above material was further treated with sodium borohydride in methanol and carboxyl groups were reduced to CH₂OH groups. The obtained MWCNT-OH (2 g) was suspended in xylene (100 ml) and then 3-aminoropropyltrimethoxysilane (APTMS) (2 ml) was added under dry nitrogen. The mixture was refluxed for 24 h and the resultant solid (ApmMWCNTs) was separated and washed with methanol to remove the unreacted residue of silvlating reagent and then dried at 80 °C. An ethanolic solution of excess terephthalaldehyde was added to the resulting nanomaterial and was refluxed for 24 h at 60 °C. The product was filtered and washed with ethanol to remove unreacted terephthalaldehyde. Afterwards, the obtained tereph-MWCNTs were suspended in ethanol (100 ml) and 2-aminothiophenol (4 mmol) was added under dry nitrogen. The mixture was refluxed for 24 h and the resulting solid (thiosal-MWCNTs) separated and was washed with methanol to remove the unreacted reagents and then vacuum dried at 80 °C. Finally, a methanolic solution of Ni(OAc)₂ and thiosal-MWCNTs was refluxed for 24 h to give Ni(OAc)₂thiosal-MWCNTs nanomaterial. The solution was filtered and the precipitate was washed several times with dichloromethane to remove any residues, and then dried in an oven at 100 °C overnight (scheme 2).

2.3. Synthesis of neat thiosal Schiff base and its complex for catalytic application

A methanolic solution of terephthalaldehyde was added to a methanolic solution of 2-aminothiophenol and stirred for ~9 h in a closed flask maintaining the temperature at ~60 °C. The yellow precipitate formed was filtered and recrystallized from hot benzene. A concentrated methanolic solution of nickel(II) acetate was added to the ligand in benzene and the mixture was refluxed for ~2 h. The precipitated complex (green solid) on cooling to room temperature was filtered, washed with hot benzene and dried in vacuum.



Scheme 2. The sequence of events in the preparation of Ni(OAc)₂thiosal-MWCNTs nanomaterial.

2.4. General procedure for the synthesis of polyhydroquinoline derivatives

The immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst (0.005 g) was added to a mixture of aromatic aldehyde (1 mmol), 1,3-dione (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.5 mmol) in a round bottom flask and the resulting mixture was stirred magnetically under solvent-free conditions at room temperature. After reaction, as observed by TLC (n-hexane/ethyl acetate: 5/2), ethyl acetate (5 mL) was added to the reaction mixture, stirred and refluxed for 10 min, washed with ethanol (5 mL) and decanted to separate catalyst from other materials (the reaction mixture was soluble in hot ethyl acetate and nano-catalyst was insoluble). The solvent of organic layer was evaporated and the crude product was purified by recrystallization from ethanol. In this study, nano heterogeneous catalyst was recycled and reused for seven times without significant loss of its catalytic activity.

2.5. Spectral data for compounds

Ethyl-2,7,7-trimethyl-5-oxo-4-(pyridin-4-yl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (*table 3, entry 8*):Yellow solid; M.p: 218-220 °C; Yield: 95%; IR (KBr): v 3285, 3203, 3073, 2941, 1689, 1622, 1480, 1223 cm⁻¹; ¹H NMR (250 MHz, DMSO-d₆): δ 1.44 (t, 3H, J = 7.2 Hz, -CH₃), 1.65 (s, 3H, -CH₃), 1.87 (s, 3H, -CH₃), 2.10 (s, 2H, -CH₂), 2.34 (s, 2H, -CH₂), 2.83 (q, 2H, J = 6.8 Hz, -CH₂), 3.65 (s, 3H, -CH₃), 4.82 (s, 1H, -CH), 7.30 (d, 2H, J = 7.4 Hz, ArH), 8.62 (d, 2H, J = 7.4 Hz, ArH), 9.20 (s, 1H, -NH); ¹³C NMR (62 MHz, DMSO-d₆): δ 26.7, 28.3, 28.7, 29.4, 31.5, 32.5, 36.2, 38.8, 39.1, 39.5, 39.8, 40.1, 40.5, 40.8, 50.4, 59.6, 102.3, 109.1, 123.2, 146.5, 146.7, 149.6, 150.5, 150.6, 155.8, 166.8, 194.7; MS: m/z = 340 [M]⁺.

*Ethyl-2-methyl-5-oxo-4-(1-phenylprop-1-en-2-yl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (table 3, entry 17):*Yellow solid; M.p: 199-201 °C; Yield: 93%) IR (KBr): v 3289, 3219, 2958, 1703, 1608, 1485, 1217 cm⁻¹; ¹H NMR (250 MHz, DMSO-d₆): δ 0.79 (t, 3H, J = 5.2 Hz, -CH₃), 1.14 (s, 3H, -CH₃), 1.51 (s, 3H, -CH₃), 2.45 (m, 6H, -CH₂), 4.32 (q, 2H, J = 7.0 Hz, -CH₂), 4.48 (s, 1H, -CH), 6.27 (s, 1H, -CH), 7.22 (m, 5H, ArH), 9.02 (s, 1H, -NH); ¹³C NMR (62 MHz, DMSO-d₆): δ 16.3, 18.4, 18.5, 21.2, 26.7, 36.4, 37.3, 38.8, 39.2, 39.5, 39.8, 40.2, 40.5, 40.8, 59.4, 111.4, 124.8, 124.9, 126.2, 128.4, 129.0, 138.4, 142.1, 145.5, 152.1, 152.5, 152.6, 167.6, 195.4; MS: m/z = 351 [M]⁺.

3. Results and discussion

3.1. Characterization of immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst

The structure of immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst was studied and identified by FT-IR, XRD, SEM, EDX, ICP, CHN and TGA analysis. In order to confirm the surface modification of MWCNTs, the FTIR spectra of the prepared materials were obtained and are shown in figure 1. The FT-IR spectrum of HOOC-MWCNTs (figure 1b) shows a strong band at 1708 cm⁻¹ and a weaker band at 1229 cm⁻¹ attributed to asymmetric stretching of COO of carboxylic acids and C-OH groups in oxidized MWCNTs, respectively, as well as a broad band about 3440–3480 cm⁻¹ assigned to O-H stretches which were not observed in the spectrum of pristine MWCNTs. As can be seen in figure 1b, in the IR spectrum of ApmMWCNTs there is a broad band at 1000–1100 cm⁻¹ assigned to Si-O stretching vibrations which were not present in pristine MWCNTs and/or HOOC-MWCNTs. The presence

of anchored propyl chain was confirmed by CH_2 stretching vibrations appearing at 2922 cm⁻¹ (asymmetric CH₂ stretch) and 2855 cm⁻¹ (symmetric stretch). The presence of these bands suggested that during the anchoring of APTMS, a condensation occurred between the OH surface groups of the oxidized MWCNTs and methoxy groups of APTMS to form the stable covalent Si-O-C linkage, leading to attachment of aminopropyl groups on the surface of MWCNTs. Thus, this treatment leads to disappearance of the bands at 1708 and 1229 cm⁻¹ and provides further evidence for the desired reaction. In the FT-IR spectrum of TerphApmMWCNTs (figure 1d), the bands observed at 1630 and 1705 cm⁻¹ were assigned to C=N and C=O vibrations due to the anchoring of the terephthaldehyde on the modified MWNTs with APTMS. In the IR spectrum of the Ni(OAc)₂thiosal-MWCNTs a sharp band at 1618 cm⁻¹ due to $v_{C=N}$ (azomethine) was shifted to lower frequencies with respect to corresponding ligand. The shift indicates involvement of azomethine nitrogen in coordination (figure 1e). In IR spectra of neat thiosal Schiff base and its neat metal complex the vibrational stretching frequency of C=N bond appears at 1632 and 1614 cm⁻¹, respectively (figures S9 and S10). Thus the attachment of thiosal Schiff base and/or its Ni(II) complex to the MWCNTs have had a small effect on stretching frequency of the imine bond.

The thermal behavior of the Ni(OAc)₂thiosal-MWCNTs was investigated by thermal gravimetric analysis (TGA). Figure 2 shows the TGA curve for the as-prepared Ni(OAc)₂thiosal-MWCNTs, presenting several weight losses from 150-630 °C. The small mass loss below 300 °C probably reflects loss of humidity. The main weight loss at 300-400 °C was assigned to the combustion of organic compounds and removing the Schiff-base from MWCNTs system which is in agreement with endothermic DTA peak in this region [12]. DTA curve demonstrates the stepwise loss in weight, where one distinct weight loss has been observed at 355 °C.

Field emission scanning electron microscopy (FE-SEM) imaging was employed to investigate the morphology of the unfunctionalized MWCNTs and products to determine the degree of nanostructured properties of the materials (figure 3). Also, figure 3b shows a SEM image of Ni(OAc)₂thiosal-MWCNTs in which nanotubes are aggregated and have retained their nanotube nature. These data also confirmed that the morphology change has not occurred during the reaction and the average diameters of these nano compounds are 150-250 nm.

The energy-dispersive X-ray (EDX) of the raw MWNTS (figure 4a) and grafted complex (figure 4b) have been compared to understand the effect of the support. The functionalization of

the MWCNTs with the Schiff base and the formation of its complex were also confirmed by the presence of C, O, N, S, Si, Ni and the corresponding metal signals in the EDX patterns of the products. The existence of nickel is confirmed by atomic absorption spectrometry as well as EDX, as can be clearly seen in figure 4.

The nitrogen content of the support was determined by CHN analysis which showed values of 2.24% for Apm-MWCNTs. Nickel content of the prepared nanomaterial was determined by inductively coupled plasma (ICP) chemical analysis which revealed the existence of 0.54 mmol.g⁻¹ nickel in the Ni(OAc)₂thiosal-MWCNTs.

Figure 5 shows the X-ray diffraction (XRD) patterns of parent MWCNTs (a) and Ni(OAc)₂thiosal-MWCNTs (b). The X-ray diffraction pattern of MWNTs bearing nickel(II) complex is similar to that for MWCNTs, indicating that the crystallinity and morphology of MWNTs were preserved during grafting method [13, 14]. Figure 5 shows that the XRD pattern of MWNTs is similar with that of highly oriented pyrolytic graphite (HOPG). The MWCNTs showed typical peak of (002), (110) and (400) at $2\theta = 26$, 43 and 53°, respectively. The (002) peak at 26°, corresponding to the inter-planar spacing of 0.340 nm, is a little greater than that of HOPG of about 0.336 nm [12].

3.2. Application of immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst

In order to find the best efficiency of the nano-sized Schiff base catalyst in the synthesis of polyhydroquinoline derivatives we tried to optimize the reaction conditions (scheme 1). As a model, the condensation reaction of 2-thiophenecarbaldehyde, dimedone, ethyl acetoacetate and ammonium acetate was studied with different amounts of the catalyst from 25-100 °C under solvent-free conditions (table 1). As can be seen in table 1, the best results were attained when the reaction was achieved in the presence of 0.005 g of nano-catalyst at room temperature (table 1, entry 7). Increasing the reaction temperature and catalyst loading did not improve the rate of the reaction (table 1, entries 8-14). In the absence of catalyst a low yield of product was acquired after 1 h (table 1, entries 1 and 2). Then we studied the solvent effect on the reaction using 0.005 g immobilized nickel(II) Schiff base complex supported on MWCNTs in various solvents (see table 2). From table 2 solvent-free reaction conditions are clearly the best choice for these reactions.

Encouraged by the significant results, several polyhydroquinoline derivatives were synthesized from Hantzsch four-component condensation of aromatic aldehydes, 1,3-diones, ethyl acetoacetate and ammonium acetate in the presence of a catalytic amount of immobilized nickel(II) Schiff-base complex supported on MWCNTs as a reusable heterogeneous catalyst under solvent-free conditions at room temperature. The results are presented in table 3. The substituents on the aromatic ring show strong effects in terms of yields under these reaction conditions. All aromatic aldehydes containing electron-releasing substituents and electron-withdrawing substituents on their aromatic ring afforded the related products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes having electron withdrawing groups were shorter than those with electron-donating groups. Furthermore, in the presence of dimedone the reaction goes faster than 1,3-cyclohexanedione.

In a proposed mechanism (scheme 3), we suggest that at first 1,3-dione is converted to its enol form by Ni(II)-Schiff base complex supported on MWCNTs and reacts with activated aldehyde via the nano-catalyst to provide intermediate I. The activated ethyl acetoacetate (via the immobilized nickel(II) Schiff-base complex supported on the MWCNTs) and ammonia (resulted from ammonium acetate) give enamine II. Then, the intermediate I and enamine II react with each other to give intermediate III. Intermediate III is converted to IV via tautomerization, and intermediate IV provides V through intramolecular nucleophilic attack of the NH₂ group to the activated carbonyl group. Finally, polyhydroquinoline derivatives form by removing one molecule of H₂O. Garden *et al.* investigated this mechanism by ESI-MS using an approach including alternate reactions with charge-tagged reagents [37-40]. According to the reaction mechanism, the presence of carbonyl groups cannot interfere with the catalytic performance.



Scheme 3. The proposed mechanism for the synthesis of polyhydroquinoline derivatives using immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst.

Reusability of the nano-catalyst was proved upon condensation of 2-thiophenecarbaldehyde, ethyl acetoacetate, dimedone and ammonium acetate. At the end of reaction, ethyl acetate was added to the reaction mixture and heated to extract the product from the substrates. This solution was washed with ethanol to separate catalyst from other materials (the product is soluble in hot ethyl acetate and nano-catalyst is insoluble). The catalytic activity of the nano-catalyst was restored for eight continuous runs (figure 6). Analysis by ICP-AES of nickel in the product after isolation of catalyst showed no loss of metal during the catalytic reaction, indicating that no metal leaching occurred. Furthermore, the XRD of the catalyst after eight cycles exposed that the structure of the catalyst maintains during the reaction.

3.3. Comparison of catalytic activity of Ni(OAc)₂thiosal-MWCNTs with known catalysts

In order to evaluate the catalytic activity of Ni(OAc)₂thiosal-MWCNTs synthesized here we compared it with previously known catalysts. Thus all previously reported catalysts that are tested in synthesis of polyhydroquinolines using model reaction between 4-chloro benzaldehyde, dimedone, ethyl acetoacetate, and ammonium acetate were compared with our catalyst, Ni(OAc)₂thiosal-MWCNTs (see table 4). In addition, the catalytic activities of Ni(OAc)₂, discrete nickel(II) Schiff base complex and also MWCNTs-COOH which are the initial reactants for synthesis of Ni(OAc)₂thiosal-MWCNTs were also compared. Table 4 shows that the yield of model reaction in the case of all catalysts (except entries 8 and 18) is lower than Ni(OAc)₂thiosal-MWCNTs and also the required reaction time for all catalysts (except entries 8 and 9) is usually much longer than our catalyst, indicating that nano-catalyst synthesized here is one of the best catalysts reported. In addition, considering that our nano-catalyst is used at room temperature, and in solvent free conditions with minimum amount of mol ratio (we remember that molecular weight of Ni(OAc)₂thiosal-MWCNTs is large and herein only 0.005 g of this catalyst has been used), we can conclude that it is in the first rank among all catalysts which are compared here. The catalytic

activity of both discrete nickel(II) Schiff-base complex and MWCNTs-COOH precursors is good (table 4). But, a comparison between the above catalysts and MWCNTs supported complexes as catalysts proves that the latter complex gave slightly higher yield of derivatives than its \precursors. Also, when we consider the second very important element, the time, then we can find that the Ni(II) Schiff-base complex immobilized on MWCNTs catalyst has better efficiency than above precursors. It should be mentioned that immobilization of transition-metal complexes on solid supports can prepare catalysts which are easy to be separated from and reused in the reaction system and which may possibly exhibit improved activities because of the support environment. Thus the excellent catalytic activity and high efficiency of Ni(OAc)₂thiosal-MWCNTs is expected.

4. Conclusion

A green and efficient immobilized nickel(II) Schiff-base complex supported on MWCNTs as a reusable heterogeneous catalyst was synthesized, considered and characterized by IR, XRD, SEM, EDX, ICP, CHN and TGA analysis. Catalytic application of **1** was studied in the synthesis of polyhydroquinoline derivatives *via* Hantzsch four-component condensation reaction of aromatic aldehydes, 1,3-diones, ethyl acetoacetate and ammonium acetate under solvent-free conditions at room temperature. Advantages of this study are reasonably low cost, high yield, short reaction time, cleaner reaction profile, reusability of nano heterogeneous catalyst and simplicity of product isolation.

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Table 1. Optimization reaction conditions in the synthesis of polyhydroquinoline catalyzed by immobilized nickel(II) Schiff-base complex supported on MWCNTs under solvent-free conditions^a.



Entry	Catalyst loading (g)	Reaction temperature (°C)	Reaction time (min)	Yield $(\%)^{b}$
	Catalyst-free	r.t.	60	15
2	Catalyst-free	100	60	17
3	0.001	r.t.	30	75
4	0.001	100	30	75
5	0.002	r.t.	30	81

6	0.002	100	30	81
7	0.005	r.t.	12	95
8	0.005	50	12	95
9	0.005	75	12	95
10	0.005	100	12	95
11	0.01	r.t.	12	95
12	0.01	100	12	95
13	0.02	r.t.	20	94
14	0.02	100	20	94

^a: Reaction conditions: 2-thiophenecarbaldehyde (1mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), ammonium

acetate (1.5mmol) and solvent free.

^b: Isolated yield.

Table 2. The solvent effect in the synthesis of polyhydroquinoline catalyzed by 0.005 g immobilized Nickel(II) Schiff-base complex supported on MWCNTs^a

S CHO Me M	e^{O} + O O O + Me^{OEt} -	NH ₄ OAc, Nano catalyst (0.005 g) r.t., Solvent (?) Me Me	S O OEt Me H Me
Entry	Solvent	Time (min)	Yield (%) ^b
1	Solvent-free	12	95
2	H ₂ O	60	20
3	C ₂ H ₅ OH	15	92
4	CH ₃ CN	15	90
5	CH ₃ CO ₂ Et	30	75
6	CH ₂ Cl ₂	60	45
7	Toluene	60	30
8	Benzene	60	30

^a: Reaction conditions: 2-thiophenecarbaldehyde (1mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), ammonium

acetate (1.5mmol), nano catalyst (0.005 g) and room temperature.

^b: Isolated yield.

Table 3. Synthesis of polyhydroquinoline derivatives using immobilized Ni(II)-Schiff base complex supported on MWCNTs^a







^a: Reaction conditions: various aldehydes (RCHO) (1mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), ammonium acetate

- ^b: Isolated yield.
- ^c: New derivatives.

^{(1.5}mmol), nano catalyst (0.005 g), solvent free and room temperature.

Entry	Amount of catalyst	Solvent	Temp (°C)	Time (min)	Yield ^b (%)	[Ref.]	
1	<i>L</i> -proline/10 mol%	C ₂ H ₅ OH/reflux	-	360	92	[36]	
2	Bismuth(III) bromide/2 mol%	C ₂ H ₅ OH	r.t	150	93	[35]	>
3	Ceric ammonium nitrate/10 mol%	C ₂ H ₅ OH	r.t	150	90	[42]	
4	K ₇ [PW ₁₁ CoO ₄₀]/1 mol%	CH ₃ CN/reflux	-	35	80	[38]	
5	Cu(II) Schiff Base Complex/1 mol%	H ₂ O	r.t	11	96	[45]	
6	HClO ₄ -SiO ₂ /50 mg	Solvent free	90	10	95	[46]	
7	SnO ₂ nanoparticle /1 mol%	C ₂ H ₅ OH	r.t	9	94	[41a]	
8	[2-MPyH]OTf/1 mol%	H ₂ O	r.t	5	97	[43]	
9	Nickel nanoparticle/ 10 mol%	Solvent free	r.t	1	90	[41b]	
10	γ -Al ₂ O ₃ -nanoparticle/ 0.2 g	Solvent free	90	8	92	[55]	
11	β -Cyclodextrin–polyurethane polymer/ 0.15 g	Solvent free	80	10	84	[56]	
12	Carbon-based solid acid/ 0.02 g	Solvent free	90	20	94	[57]	
13	Titanium Dioxide Nanoparticles/10 mol%	C ₂ H ₅ OH	80	120	90	[58]	
14	FeF ₃ / 5 mol%	C ₂ H ₅ OH	75	60	90	[59]	
15	clay supported Ni ⁰ nanoparticles/25 mg	Solvent free	r.t	15	88	[60]	
16	Aluminum Phosphate [AlPO ₄ (H)]/ 10 mg	Solvent free	90	15	90	[61]	
17	PPA-SiO ₂ / 0.03 g	Solvent free	80	45	92	[62]	
18	guanidine hydrochloride organocatalyst/10mol%	C ₂ H ₅ OH	r.t	180	97	[63]	
19	Ionic liquid/ 10 mol%	C ₂ H ₅ OH	40	12	93	[64]	
20	ZnO-nanoparticle/ 10 mol%	Solvent free	r.t	25	95	[65]	
21	Hf(NPf ₂) ₄ / 1 mol%	perfluorodecalin	60	180	93	[66]	
22	[(CH ₂) ₄ SO ₃ HMIM][HSO ₄]/0.25 mmol	C ₂ H ₅ OH/reflux	-	95	83	[67]	
23	Scolecite/ 200 mg	C ₂ H ₅ OH/reflux	-	50	95	[68]	
24	Zinc Oxide/ 10 mol%	C ₂ H ₅ OH	80	60	92	[69]	
25	ZrCl ₄ /5 mol%	C ₂ H ₅ OH	r.t	120	88	[70]	
26	<i>P</i> -TSA/ 10 mol%	C ₂ H ₅ OH	r.t	120	90	[71]	
27	Cerium(IV) ammonium nitrate/ 10 mol%	C ₂ H ₅ OH	r.t	150	90	[72]	

Table 4. Comparison of various catalysts in the four-component Hantzsch condensation for synthesis of polyhydoquinolines.^a

28	$K_5 CoW_{12}O_{40}.3H_2O/\ 0.01\ mol\%$	Solvent free	90	15	93	[73]	
29	L-proline/0.1 mmol	C ₂ H ₅ OH	r.t	30	91	[74]	
30	Ni(OAc) ₂ / 0.005 g	Solvent free	r.t	35	86	-	
31	Ni(OAc) ₂ thiosal Schiff-base complex/ 0.005 g	Solvent free	r.t	10	95	-	
32	MWCNTs-COOH/ 0.005 g	Solvent free	r.t	10	94	-	
33	Ni(OAc) ₂ thiosal-MWCNTs/ 0.005 g	Solvent free	r.t	7	97	_	>

^a: Reaction conditions: 4-chloro benzaldehyde (1mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), ammonium acetate

(1.5mmol).

^b: Isolated yield.

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Figure 1. FT-IR spectra of (a) MWCNTs, (b) HOOC-MWCNTs, (c) ApmMWCNTs, (d) TerphApmMWCNTs and (e) Ni(OAc)₂thiosal-MWCNTs.



Figure 2. TGA and DTA curves of Ni(OAc)₂thiosal-MWCNTs.



Figure 3. The SEM images of (a) MWCNTs and (b) Ni(OAc)₂thiosal-MWCNTs.

AND WANT



Figure 4. EDX diagram of (a) MWCNTs and (b) Ni(OAc)₂thiosal-MWCNTs.

Figure 5. XRD pattern of the MWCNTs (a) and the Ni(OAc)₂thiosal-MWCNTs (b).

Figure 6. Reusability of immobilized nickel(II) Schiff-base complex supported on MWCNTs as a heterogeneous catalyst in 12 minutes.

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Graphical abstract

