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Investigation of Catalytic Activity of Pillared-layer Ni (II) Metal-Organic Framework Derived NiO Nanoparticles for Aromatization of Hantzsch 1,4-Dihydropyridines

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Abstract

The pillared-layer metal-organic framework of $Ni_2(BTEC)(bipy)_3.3DMF.2H_2O$ (BTEC = 1,2,4,5-benzenetetracarboxylate; bipy = 4,4′-bipydine; DMF =N,N′-dimethylformamide) was prepared, characterized and used as a precursor for preparation of NiO nanoparticles. The morphology and structure of NiO nanoparticles were characterized by XRD, SEM, FT-IR and EDX techniques. It was found that the synthesized MOF and NiO nanoparticles catalyze the aromatization of 4-substituted Hantzsch 1,4-dihydropyridines (R= Ph, Me, H) with 100% conversion and 100% selectivity toward the desired products.

Keywords: Pillared-layered NiMOF; NiO nanoparticles; Aromatization.

Introduction

1,4-dihydropyridines (1,4-DHPs) are class of N-heterocyclic compounds have been gained great interest as pharmaceuticals in the field of medical chemistry [1]. These compounds are analogs of NADH coenzymes and widely used as calcium channel blockers to treat cardiovascular diseases [2]. The metabolic route of these drugs involves their oxidation to the corresponding pyridine derivatives by the action of cytochrome P-450 in the liver [3]. Additionally, the oxidation of Hantzsch 1,4-dihydropyridines provide an access to pyridine derivatives which are important as class of bioactive compounds and organic chemistry intermediates [4]. Pyridines display a considerable biological and pharmacological properties such as antitumor [5], Antiplasmodial [6], anti-inflammatory [7], anti-proliferative [8] and antimicrobial [9]. Therefore, much attention has been devoted to aromatization of 1,4-dihyropiridines.

Numerous reagents and procedures have been developed for these purposes such as $KMnO_4$ [10], SeO_2 [11], $KBrO_3/SnCl_4\_5H_2O$ [12], H_2O_2/MoO_3 [13], $H_2O_2/Co(OAc)_2$ [14], Co-naphthenate/O_2 [15], nicotinium dichromate [16], H_2O_2/Si-Zr-Mo [17], S-nitrosoglutathione [18], NO [19], palladium catalyst [20] and peroxydisulfate–cobalt (II) [21], graphite oxide[22], radical cation salt [23], cupric bromide [24], acetic acid [25], human hemoglobin [26], iodobenzene diacetate [27], trinitratocerium (IV) bromate [28], molecular iodine [29],

Metal-organic frameworks (MOFs) have potential applications in gas separation and storage, sensors, drug delivery [30-31] and catalysis for a variety of organic

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transformations, such as catalytic production of nitric oxide [32], ketalization reaction [33], Henry reaction [34], Friedel–Crafts reaction between pyrroles and nitroalkenes [35], Oxidation [36], cycloaddition of CO_2 with epoxides [37], and Suzuki cross-coupling [38], Sonogashira reaction [39]. Based on our knowledge, there has been no report on aromatization of 1,4-dihydropyridines by MOFs in literature. Metal organic frameworks has been proven to be a proper precursor for the preparation of metal oxides with controlled shapes and morphologies in heterogeneous catalysis application [40]. Nickel oxide nanoparticles due to low cost, unique chemical properties, stability and easy preparation have been used as photocatalyst [41], dehydrogenation [42], methan reduction and carbon nanofiber formation[43] and so on.

In this study, pillared-layer Ni (II) metal-organic framework synthesized, characterized and used as precursor for preparation of NiO nanoparticles. The catalytic activity of Ni-MOF and prepared NiO nanoparticles were investigated for the aromatization of 4-Substituted Hantzsch 1,4-dihydropyridines (R= Ph, Me, H).

Materials and Methods

Materials and instrumentation

All the chemicals were obtained from Merk Chemical Company and used without further purification. The products were analyzed by GC and GC-Mass using an Agilent 6890 series, with FID detector, HP-5.5% phenylsiloxane capillary column and Agilent 5973 network, mass selective detector HP-5, MS 6890 network GC system, respectively. X-ray diffraction (XRD) data were recorded with Rigaku D/Max-2550 PC diffractometer (Japan) with nickel filter and CuK(α) radiation at 40 kV and 30 mA. FT-IR spectra were recorded on a Brucker Tensor 27 spectro-photometer. The nanostructure of the sample was analyzed by scanning electron microscopy (SEM; S-4160 Hitachi).

Preparation of $Ni_2(BTEC)(bipy)_3.3DMF.2H_2O$ metal organic framework and NiO nanoparticles

$Ni_2(BTEC)(bipy)_3.3DMF.2H_2O$ metal organic framework was prepared as reported [44]

with some modification. A solution of H_4BTEC (0.051 g,2.0 mmol), 4,4-bipy (0.115 g, 6.0 mmol), and $Ni(NO_3)_2.6H_2O$ (0.116 g, 4.0 mmol) in 10 ml DMF was sealed in a 25 mL autoclave and kept at 110 °C for 3 days. The obtained green crystalline powders were washed with DMF and EtOH, and dried under vacuum at 60 °C. Found: C, 53.40; H, 4.71; N, 11.59, as reported in literature [44], and then calcinated at 800 °C for 8h to prepare NiO nanoparticles.

Synthesis of 1,4-Dihydropyridine

1,4-dihydropyridines (R= H, Me, Ph) were prepared according to the procedure

reported previously [45].

Dehydrogenation of 1,4-dihyropyridine general procedure

In a typical procedure, 1,4-DHP (30 mg, 0.09 mmol) and catalyst (30 mg) were added to CH_3CN (15 mL), H_2O_2 (2 mL, 30%) and the mixture was refluxed at 60 °C for 8h. It was then filtered and the filtrate was subjected to GC and GC-Mass analysis.

Results and Discussion

Characterization of Ni(BTEC)BPY and NiO nanoparticles

The overall XRD patterns of the Ni(BTEC)BPY before and after using as catalyst are shown in Figure 1 (a-b) respectively. The XRD pattern of Ni(BTEC)BPY

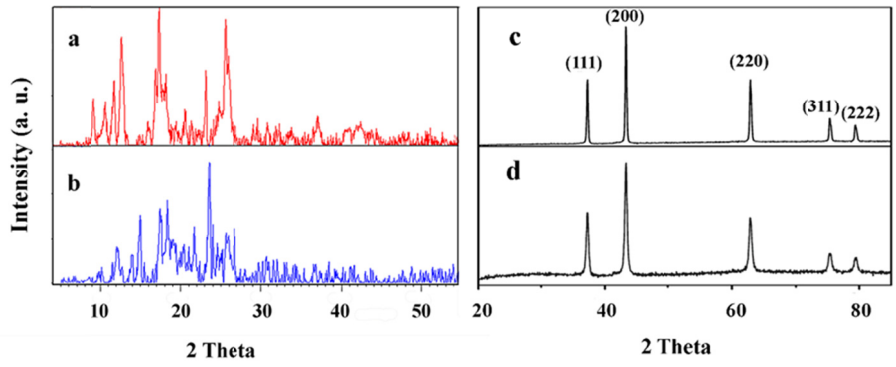


Figure 1. XRD pattern of (a) fresh and (b) reused Ni(BTEC)BPY structure, (c) fresh and (d) reused NiO nano particles.

(Figure 1a) is in good agreement with that previously reported in the literature [44]. Calcination of the Ni(BTEC) BPY particles at 800 ˚C for 8h in air produced NiO nano particles. The XRD patterns of the as prepared NiO nano particles before and after using as catalyst are shown in Figure 1 (c-d) respectively. All the diffraction patterns are consistent with the pure standard cubic NiO (JCPDS card 04-0835, space group: fm3m).

The SEM images of Ni(BTEC)BPY revealed that the pillared-layer structure with spherical structure about 89 nm are formed (Figure 2), The SEM and elemental mapping and of NiO nanoparticles are also shown in Figure 3 (a-c) respectively. Based on the obtained results NiO nano particles with pillared-layer structure containing spherical nano particles about 80 nm and Ni and O elements are observed by elemental mapping (Figure 3a-c).

FT-IR spectra of, 1,2,4,5-benzenetetracarboxylic acid, 4,4′-bipyridine, fresh and reused Ni(BTEC)BPY and NiO nanoparticles are shown in Figure 4 (a-e) respectively. The strong peak at 1702 cm^{-1} in the spectrum of the 1,2,4,5-benzenetetracarboxylic acid (Figure 4a) is assigned to the C=O stretching vibrations of free carboxylic acids, this peak was shifted to 1690 cm^{-1} (Figure 4c) in the spectrum of the Ni(BTEC)BPY, observing a strong peak at 1663 cm^{-1}, in the spectrum of Ni(HBTC)BPY indicating the deprotonation of COOH groups of 1,2,4,5-benzenetetracarboxylic acid upon the

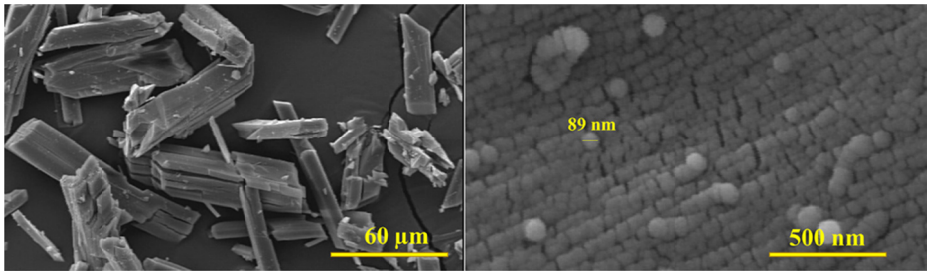


Figure 2. SEM image of Ni(BTEC)BPY with two magnification.

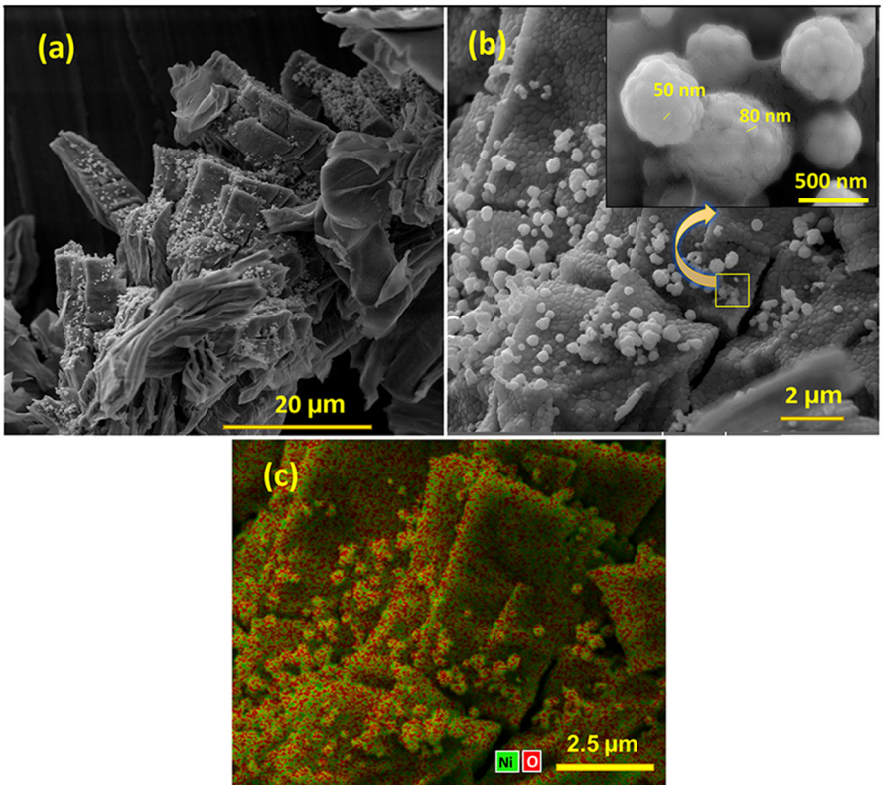


Figure 3. (a,b) SEM images (c) elemental mapping of NiO nanoparticles.

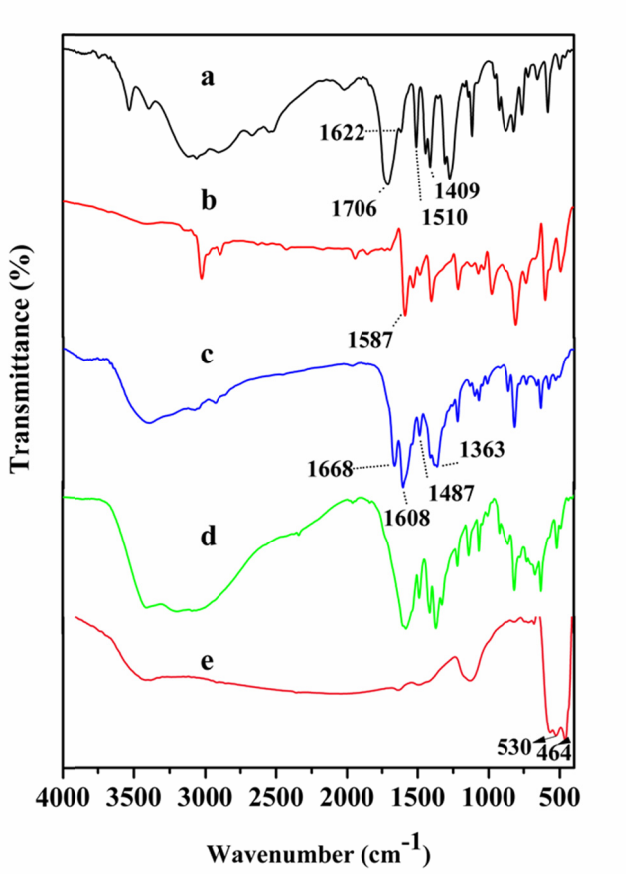


Figure 4. FT-IR spectra of the (a) 1,2,4,5-benzenetetracarboxylic acid (b) 4,4'-bipyridine (c) fresh and (d) reused Ni(BTEC)BPY (e) NiO nanoparticles.

reaction with nickel ions [46]. The C=N stretching vibrations in the 4,4′-bipyridine is observed at 1588 cm^{-1} (Figure 4b) which is decreased to 1498 cm^{-1} in the spectrum of the Ni(BTEC)BPY, confirming the coordination of the nitrogen with metal ions. A doublet vibrations appeared at 530 and 464 cm^{-1} in the spectrum of NiO nanoparticles are attributed to the Ni-O stretching vibrations (Figure 4d) [47]. The EDAX spectrum of NiO nanoparticles shows the presense of Ni and O elements (Figure 5) which are consistent with those also reported in map results.

Catalytic activity

The catalytic activity of Ni(BTEC)BPY for oxidative aromatization of the 1,4-DHP (R= Ph) was studied in the absence and presence of H_2O_2 as oxidant in different solvents and times. The results are given in Table 1, it was found that aromatization reaction proceeds with 100% conversion and 100% selectivity in acetonitrile and H_2O_2 within 6h. Reaction conditions based on the effect of amounts of catalyst was optimized and results are given in Figure 6. Based on the obtained results (Table 1), it was found that in absence of catalyst in 8h 1,4-DHP is converted to the corresponding pyridine with 25% conversion and 100% selectivity. With increasing the amount of catalyst to 0.03g the reaction completed with 100% conversion and 100% selectivity

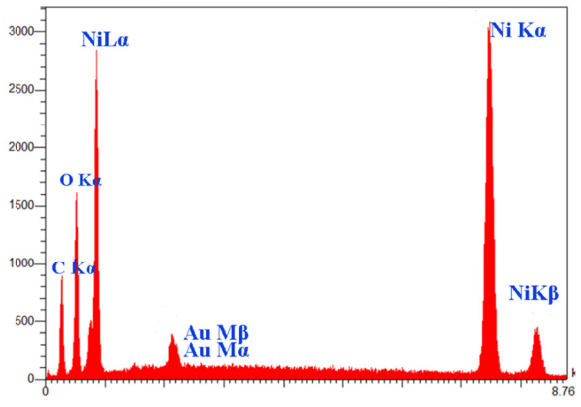


Figure 5. The EDX s of NiO nanoparticles

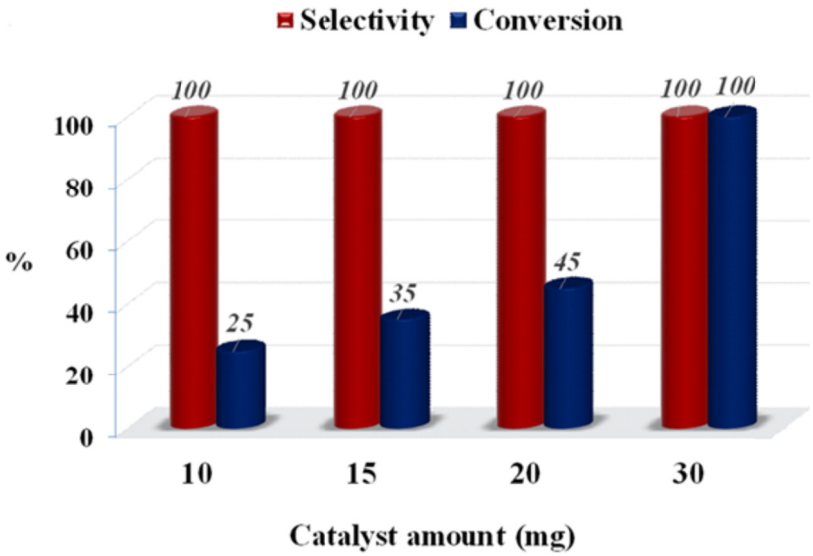
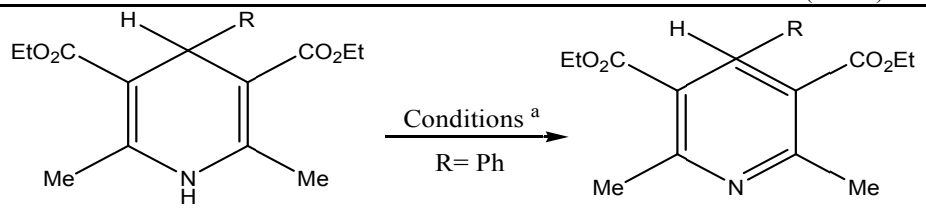


Figure 6. The effect of catalyst amount on aromatization of DHP with Ni(BTEC)BPY

Table 1. The effect of solvent and reaction time on aromatization of DHP with Ni(BTEC)BPY.



Entry	Solvent	Time(h)	Conversion (%)	Selectivity (%)
1	EtOH	6	0	0
2	CH_3CN	6	0	0
3	CH_2Cl_2	6	0	0
4	CCL_4	6	0	0
5	EtOH	24	33	36
6	CH_3CN	24	35	100
7	CH_2Cl_2	24	0	0
8	CCL_4	24	63	44
9	EtOH + H_2O_2	6	35	100
10	CH_3CN+ H_2O_2	6	100	100

[a] Conditions: DHP (0.03 mmol), catalyst (30 mg), H_2O_2 (2 mL).

(Figure 6). Therefore, catalyst has important role in dehydrogenation process. The results of optimization of reaction time is shown in Figure 7. It was also found that increasing time from 1 to 6 h, conversion and selectivity were increased to 100% after 6 hours. In addition, the established optimized reaction conditions were then tested on DHPs with R = H and Me, which converted to the corresponding pyridines in 1 and 2

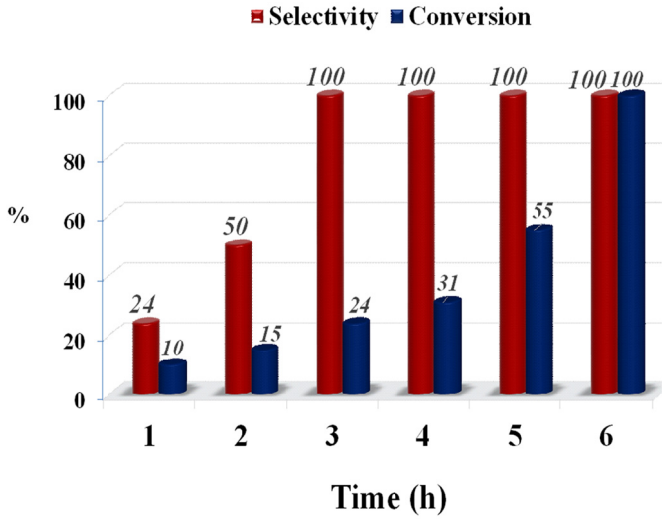


Figure 7. The effect of reaction time on aromatization of DHP with Ni(BTEC)BPY

Table 2. The effect of R group on dehydrogenation of DHP derivatives with Ni(BTEC)BPY.

Entry	R	Solvent	Time (h)	Conversion (%)	Selectivity (%)
1	Ph	CH_3CN	6	100	100
2	H	CH_3CN	1	100	100
3	CH_3	CH_3CN	2	100	100

[a] Conditions: DHP (0.03 mmol), catalyst (30 mg), H_2O_2 (2 ml).

Table 3. The effect of R group on dehydrogenation of DHP derivatives [a] with NiO nanoparticles.

Entry	R	Solvent	Time (min)	Conversion (%)	Selectivity (%)
1	Ph	CH_3CN	30	100	100
2	H	CH_3CN	1	100	100
3	CH_3	CH_3CN	1	100	100

[a] Conditions: DHPs (30 mg), catalyst (15 mg), H_2O_2 (2 mL)

hours respectively. As seen in Table 1, when reaction was carried out in solvents such as EtOH, CH_3CN, CCL_4 (entries 1, 2, 3) without using H_2O_2 no product was formed, but by increasing time from 6 to 24 hours, in CH_3CN and CCl_4 the reaction conversion were increased from 35 to 63% with decreasing selectivity (entry 6, 8). Using CH_2Cl_2 in similar conditions no product was formed (entry 7). Based on the obtained results, the presence of catalyst, oxidant, and the type of solvents has essential effect on formation of desired products. In the next step, the derived NiO nanoparticles formed from pillared Ni MOF and used as catalyst for aromatization of the DPHs. The optimized reaction conditions are shown in Figures 8, 9.

As seen in these Figures and Tables 2 and 3 the rate of reaction is much faster than with NiMOF. In which after 30 minutes with 15 mg of catalyst 100% conversion and selectivity was observed. In last by changing R to H or methyl the rate of reaction was so fast and the reactions were completed in 1 minutes. FT-IR spectra of the reused Ni(BTEC)BPY after the first run exhibited a similar absorption as compared to that of the fresh catalyst (Figure 4.d), but the XRD result of the reused catalyst after the first run indicated that the crystallinity of the catalyst slightly changed during the course of the reaction (Figure 1.b). The XRD of NiO nanoparticles before and after reaction were similar and no desorption was observed during the course of reaction. On the other hand the filterate solution did not show any catalytic activity which should be due to the heterogenity character of the catalyst. Therefore, it seems NiO nanoparticles are a good candidate for

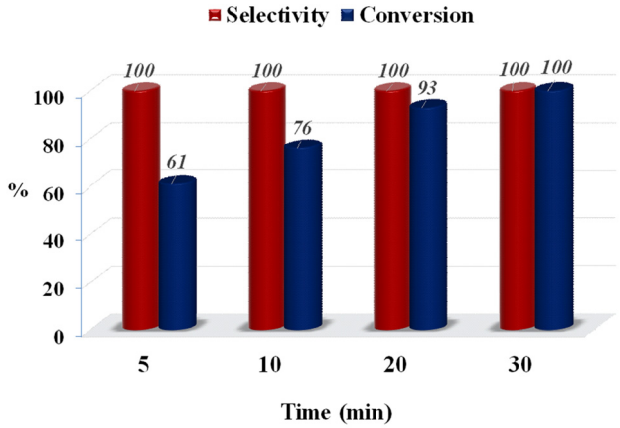


Figure 8. The effect of reaction time on aromatization of DHP with NiO nanoparticles.

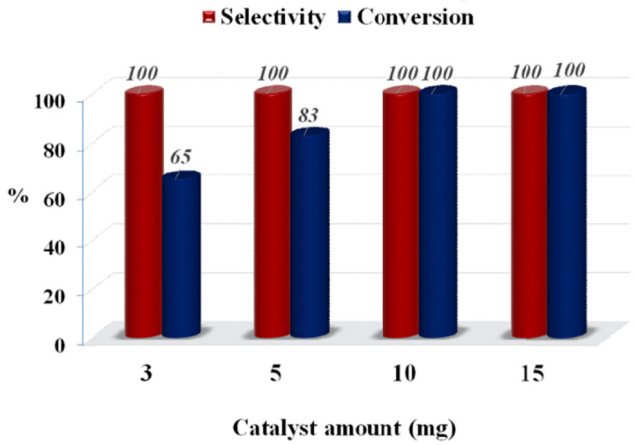


Figure 9. The effect of catalyst amount on aromatization of DHP with NiO nanoparticles.

aromatization reactions without loosing catalytic activity after four runs.

The catalytic activity of NiO as nanopartcles was compared with other reported systemes [14,17,24,25,48-50]for aromatization of Hantzsch 1,4-dihydropyridines (Table 4). It was found that the the conversion, selectivity and reaction time toward the corresponding products with 100% conversion and 100% selectivity is considerable.

Conclusions

Pillared Ni(BTEC)BPY was synthesized from the reaction of 1,2,4,5- benzenetetracarboxylic acid, nickel nitrate hexahydrate, and 4,4-bipyridine by a solvo-thermal method and then calcinated at 800 ˚C for preparation of NiO nanoparticles. The prepared samples were characterized by XRD, FT-IR, SEM, mapping and EDX techniques. The NiO nanoparticles were formed as

Table 4. Comparison of results of dehydrogenation of DHP derivative (R=Ph) with NiO nanoparticles with previously reported catalysts.

Entry	Catalyst	Conversion[a] (%)	Selectivity (%)	Time (min)	Ref
1	MOF derived NiO nanoparticles	100	100	30	This work
2	aqueous H_2O_2–acetic acid	92	100	60	25
3	cupric bromide	93	98	60	24
4	$SiO2/P_2O_5$-SeO_2	90	100	30	48
5	FePcS-NH_2 -SiO2(TBHP)	35	88	6h	49
6	$NaClO_2$	96	100	30	50
7	Cobalt(II) Acetate	97	100	30	14
8	Si-Zr-Mo nanocomposite	100	100	3	17

spherical nanoparticles with average diameter of 80 nm. Investigation of catalytic activity revealed that NiO nanoparticles are more active than the prepared NiMOF as catalyst for aromatization of Hantzsch 1,4-dihydropyridines toward the corresponding products with 100% conversion and 100% selectivity.

Acknowledgements

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