

Cycloaddition of Propargylic Amines and CO₂ by Ni@Pd Nanoclusters Confined Within Metal–Organic Framework Cavities in Aqueous Solution

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Abstract

The bio-metal–organic framework (bio-MOF) notion along with nanoparticles catalysts of Ni@Pd core–shell magnetic for carbon dioxide conversion is made by L-glutamic acid that is the natural substitute for combinatorial ligands, and illustrated their catalytic effect, in the propargylic amines cyclization with carbon dioxide for obtaining 2-oxazolidinones, completed to the correlation of structure–DFT. This nano Ni@Pd that consists of catalyst is detected using ICP, XRD, TGA, TEM, FT-IR, and VSM. The zinc-glutamate-MOF or ZnGlu is properly proved as the MOF catalyst in the case of the propargylic amines cyclization with carbon dioxide for obtaining 2-oxazolidinones, in addition, its performance is compared to those of outstanding synthetic MOFs stated in the method. The produced catalyst done even at moist state, is thermally as well as chemically firm; easily separable, heterogeneous, because of high selectivity of it, lack of mixture solvents, and also simple catalyst recovery using outside magnet. It is recycled until ten times. Ni@Pd/ZnGlu MNPs dramatically improves the availability of the nanoparticle levels in comparison whit the common substrate because of its 3D hierarchical construction. Ni@Pd/ZnGlu MNPs, because of their economic environmental and economic parameters, are considered as the future of MOF chemistry in industry.

Graphic Abstract

Cycloaddition of propargylic amines and CO_2 by Ni@Pd nanoclusters confined within metal–organic framework cavities in aqueous solution.



Keywords Heterogeneous catalyst \cdot One-pot synthesis \cdot Green chemistry \cdot CO₂ \cdot 2-Oxazolidinone

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1 Introduction

Recently, expansion of green approaches according to chemical consolidation of carbon dioxide is received a big deal of concern owning to carbon dioxide can be utilized as a cheap, renewable, and safe C₁ structure block to produce proper organic materials. Different beneficial chemicals, like cyclic carbonates [1–3], polycarbonates [4], urethanes [5], methanol [6], dimethyl carbonate [7–10], formic acid [11], etc. are provided utilizing CO_2 . One of the beneficial expansion in which carbon dioxide are used as a layer is via the carboxylative cyclization from propargylic amines with carbon dioxide for obtaining 2-oxazolidinones [12–15] 2-oxazolidinones significant heterocyclic chemicals that has a significant pattern as chemical intermediates [16] as well as chiral auxiliaries [17] in the case of organic production, and also as antibacterial medicines [18] in green chemistry. The carboxylative cyclization in the case of propargylic amines by carbon dioxide that uses for a main clean economic reaction is known as one of the most appropriate instances of carbon dioxide consolidation to achieve 2-oxazolidinones.

Metal-Organic Frameworks (MOF) are achieved great respond from researchers because it prepares an extensive range of usages in term of gas carbon dioxide capture, storage, catalysis research, separation, and guest dependent luminescence fields [19-26]. The eco-friendly MOFs has been commonly for feited because of the combinatorial nature of ligands. Toxic ligands or organic solvents stay in lattices of MOF; trace areas are discovered even since activation. Bio-MOFs are anticipated as the future of MOF materials in an environmentally safe community [27-31]. Because of richness of amino acids in amino carboxylate or functional classes in chains, amino acids possess the heritage of amino acid within cycloaddition catalysis at fresh and improved states [32-35]. Heterogeneous catalysis utilizing MOF-supported small metal nano-particles (NPs) or nanocarbons (NCs) are achieved growing research consideration due to the nanopores of MOFs may not just serve as formats to produce monodisperse metal of NPs/NCs, however, provide micro environments, which can apply selectivity control upon the enclosed NPs/NCs into catalytic reactions. The arrangement of metal NPs/NCs within MOFs is performed using chemical vapour evidence utilizing organometallic precursors within the gas [36, 37]. Palladium NPs have special importance between the noble metals due to their premier catalytic efficiency [38-40]. Palladium NP nanocatalysts are receiving high consideration because of their catalytic activity during the wastewaters treatment having 4-NP or 4-CP pollutants [41–44].

Virtually, most catalytic reactions of noble metal NPs occur only onto the NPs level and a great atom fraction within the core are catalytically inactive. Therefore, to make a major percent of noble metal atoms available by catalysis and for decreasing the utilize, the interior noble metal atoms may be changed using different non-noble metals like Ni, Co, and Fe to decrease the utilize of noble metal but removing the total efficiency of the catalyst. Moreover, the existence of Ni, Fe, and Co in hybrid, core-shell NPs possess proper magnetic separability, solvent adaptability, stability, and catalytic activity [45–47]. Whole these characteristics greatly increase the potential usage of considered catalysts. Hence, promising noble metal catalysts of NPs with inactive cores, impressive recoverable, and great catalytic activities characteristics are acutely rare [48–51].

The present work attained to expand new catalysts and noble metal NPs along with proper dispersed high accessibility for the procurement of 2-oxazolidinone using reaction of propargylic amine and carbon dioxide at the eco friendly states. Hereon, we select a proteinogenic amino acid and L-glutamic acid as well as only spacer of MOF material. ZnGluis utilized as a novel supporting substance to avouch Ni@Pd NPs for achieving Ni@Pd/ZnGlu MNPs with increased availability for active levels and high level zone. ZnGlu showed not just proper rate of catalytic reaction, however, great reusability for the catalytic reaction. The great activity of it is due to its high approachability as well as low possibility of the compression and leaching of the Nps on the Ni@Pd/ZnGlu support approach (refer to Scheme 1).



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1} & \mbox{Synthesis of 2-oxazolidinone on the surfaces of Ni@Pd/ZnGlu} \\ \end{tabular}$

2 Experimental

2.1 Materials and Methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus and are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. The particle size and structure of nano particle was observed by using a Philips CM10 transmission electron microscope operating at 100 kV. Powder X-ray diffraction data were obtained using Bruker D8 Advance model with Cu ka radiation. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min⁻¹ under nitrogen. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Mass spectra were recorded on Shimadzu GCMS-QP5050 Mass Spectrometer.

2.2 General Approach About the Production of ZnGlu

Single crystals as well as bulk powder of zinc-glutamate-MOF are singly achieved of the similar reaction compound. For a aqueous solution of 30 mL stirred of 0.294 g (2 mmol) L-glutamic acid along with 0.200 g (5 mmol) NaOH is released 0.575 g (2 mmol) zinc sulfate heptahydrate within 15 mL water using a dropping funnel. Immediate precipitation resulted in the by utilizing vessel being hold in to an oil bath under the temperature of 100 °C; thenceforward the temperature of oil bath is enhanced increased to the temperature of 140 °C. The solution along with the precipitate is returned within in the oil bath at 6 h as well as the white sudden is removed off provided hot. The refine achieved is evaporated for decreasing the volume nearly about 10 mL and hold at stable temperature of 25 °C at a few days for obtaining X-ray diffraction modality Zn(H₂O) (C₅H₇NO₄).H₂O crystals. The precipitate achieved in the bulk is additionally dried at the presence of air and under the temperature of 25 °C and is defined as ZnGlu(C) and further evaluated in the case of structural resemblance of the bulk-produced catalyst to single crystals. The catalyst has been dried under temperature of 25 °C [52].

2.3 General Approach About the Synthesis of Ni@ Pd/ZnGlu

Ni@Pd/ZnGlu NPs are provided using reaction of ZnGlu to 49.7 mg nickel(II) acetate tetrahydrate (0.0002 mol) and

0.0534 g palladium(II) bromide (0.0002 mol) are mixed to 18.0 mL OAm and 0.3 mL TOP under the temperature of 25 °C. The reaction is heated to 245 °C at a gentle flow of argon for 1 h. After that the Ni@Pd/ZnGlu is separated of the reaction compound using a magnet and then washed for many times by deionized water as well as acetone. Eventually, Ni@Pd/ZnGlu is dried at vacuum and the temperature of 50 °C [45].

2.4 General Approach About the Synthesis of 2-Oxazolidinone

In a Schlenk-tube are properly added 1.0 mg Ni@Pd/ZnGlu MNPs. In addition, 1 mmol propargylic amine at the presence of argon atmosphere and the within Schlenk-tube is replaced to 1.5 MPa carbon dioxide. The carboxylative cyclization of the propargylic amine in the presence of carbon dioxide performed using the stirring of the yielded mixture under the temperature of 25 °C at solvent-free state and also visible light irradiation by a 15 W CFL at 2 h. Until end of the reaction, the advance of the reaction is evaluated using TLC while the reaction is ended, methanol as well as dichloromethane are released to the reaction compound and the catalyst is separated using a magnet. After that the solvent is separated of solution at decreased pressure and the yielding product cleaned using recrystallization by methanol.

3 Results and Discussion

After load ions of Ni@Pd NPs onto ZnGlu, which is like to an eco-friendly MOF, propargylic amines cyclization to CO_2 to obtain 2-oxazolidinones is used. The results suggest the amine groups within ZnGlu can forcefully assistance the loading of metal NPs as stated in other different MOFs. This view is just like to the production and metal NPs/NCs encapsulation in the dendrimers of poly(PAMAM). Within PAMAM dendrimer, the interplay among metal pioneers and the internal amino teams of the dendrimer was reliable to be the basis proof to load metal in the dendrimer.

Since loading of Ni@Pd in ZnGlu, the X-ray diffraction (XRD) of powder is utilized to examine that whether the Ni@Pd NPs fraught on ZnGlu as yet protected their crystal structure. The XRD schemes of the as-produced ZnGlu (refer to Fig. 1b) matched properly to the obtained XRD patterns (refer to Fig. 1a). Since the loading on Ni@Pd NPs, there is no exterior disadvantage of Bio-MOF in XRD schemes (refer to Fig. 1c). XRD evaluation may prepare situation for the Ni@Pd NPs composition. Figure 1c shows that Ni@Pd NPs represented sharp peaks for Pd (111), Ni (111), Pd (200) and Pd (220) as well as Pd (311) that also inquire the existing fcc-Pd and also fcc-Ni.

Fig. 1 XRD analysis of (a) simulated ZnGlu; (b) ZnGlu; and (c) Ni@Pd/ZnGlu



Fig. 2 SEM images of a ZnGlu; and b Ni@Pd/ZnGlu; TEM images of c ZnGlu; and d Ni@ Pd/ZnGlu



The morphology along with the produced ZnGlu sizes, and Ni@Pd/ZnGlu NPs are evaluated using TEM and SEM analyses. The mean microspheres diameter is in the range of 100–120 nm (refer to Fig. 2a, b). It showed that the ZnGlu is loaded to well-dispersed Ni@Pd nanoparticles (as can be seen in Fig. 2c, d). More investigation of the TEM scheme of the reproduced catalyst indicates that the Ni@PdNPs fully the ZnGlu are properly scattered. It is found that when Ni@Pd/ZnGlu NPs performs as a spatial about extremely active and soluble Ni@Pd NPs, it can additionally act as a nanoscaffold for recapturing the Ni@Pd NPs within the tree construction of ZnGlu, so barricading Ni@Pd compaction.

The interplay of Ni@Pd as precursors to the $-NH_2$ materials of glutamate is additionally proved using FT-IR spectra. As can be seen in Fig. 3 that showing the FT-IR spectra, the peaks are shown close to 1255 cm⁻¹ which have bright intensity variations like the Ni@Pd loading on ZnGlu is enhancing. In addition, two different peaks are observed near 1642 and 1424 cm⁻¹ that possess clear intensity variations like the Ni@Pd loading is enhanced. The peak close to 1089 cm⁻¹ may be ascribed to the $-NH_2$ cutting as well as rocking

vibration. The intensities in the case of nitrogen–hydrogen asymmetric stretching peak of vibration near 3640 cm⁻¹, and nitrogen–hydrogen symmetric stretching peak of vibration close to 3561 cm⁻¹ (as observed in Fig. 3a) reduce dramatically with the increasing Ni@Pd loading, and red variations to 3324 and 3219 cm⁻¹ in the case of the former one (refer to Fig. 3b).

The TG pattern about Ni@Pd/ZnGlu NPs is found and illustrated in Fig. 4. In term of Ni@Pd/ZnGlu simple, among 50 °C and 280 °C to 5% lost weight relating to water physically adsorbed. The amino functionalized analogues of Ni@ Pd/ZnGlu indicated dramatic weight losses of 21% to 24% under the temperature of 400 °C, likely because of ligand disintegration. As can be illustrate in Fig. 4, a considerable weight loss stage emerged under the temperatures between of 550 and 600 °C, that is related to the material oxidizes decomposition. Ni@Pd/ZnGlu NPs indicated a promising thermal consistency under reaction temperature.

Figure 5 shows magnetization curves about the super paramagnetic conduct of the Ni@Pd nanoparticles and nanocatalyst of Ni@Pd/ZnGlu. The magnetic saturation amounts



Fig. 3 FTIR spectra of (a) ZnGlu; and (b) Ni@Pd/ZnGlu



related to the NPs of Ni@Pd and nanocatalyst of Ni@Pd/ ZnGlu were 43.3 and 24.7 emu g⁻¹. Hence, the NPs of Ni@ Pd enhanced Ni@Pd/ZnGlu nanocatalyst can be properly removed from the solution utilizing an outside magnetic force, and can be utilized and also recycled.

XPS can be used for investigating the chemical parts of the MNPs site of Ni@Pd/ZnGlu MNPs. A pattern of XPS in the case of the as gathered catalyst are illustrated in Fig. 6. Peaks corresponded to N, Pd, Zn, O, C, and Ni can be observed in Fig. 6. The N1s spectrum related to L-glutamic acid indicates two parts on the core site spectrum deconvolution at 399.4 as well as 401 eV; properties of the C–NH₂ group. ZnGlu possess N1s peaks close to 399.8 and 401.5 eV; the slight change than higher binding energy can be due to coordination of Zn–NH₂. Moreover, XPS spectrum for Pd3d indicates a match indicative of metallic Pd.

It is known that the Ni@Pd immobilization on the level of ZnGlu NPs can cater a proper dispensation of catalytically active Ni@Pd parts upon the support and reinstates the Ni@Pd NPs in the chemical reaction as well as supports the

Fig. 6 XPS spectra of Ni@Pd/ ZnGlu MNPs



Table 1Synthesis of2-oxazolidinone by Ni@Pd/ZnGlu MNPs in differentsolvents

Entry	Solvent	Yield (%) ^a			
1	H ₂ O	53			
2	MeOH	46			
3	EtOH	42			
4	i-PrOH	49			
5	THF	18			
6	EtOAc	38			
7	DMF	17			
8	Toluene	6			
9	CH ₂ Cl ₂	35			
10	CHCl ₃	38			
11	DMSO	39			
12	CH ₃ CN	-			
13	Dioxane	-			
14	n-Hexane	-			
15	Solvent-free	95			

Reaction conditions: propargylic amine (1 mmol), CO_2 2.0 MPa, Ni@Pd/ZnGlu MNPs (2 mg), and under visible light irradiation using a 32 W CFL, after 3 h

^aIsolated yields

Ni@Pd NPs from compression. Moreover, the hydrophilic nature of supported ZnGlu prepares an averages of proper dispersion of ZnGluNPs in aqueous medium to expand this apparatus as a semi-homogeneous catalyst of Ni@Pd about organic reactions at solvent-free like a safe and green states. To demonstrate this, the Ni@Pd/ZnGlu MNP catalytic activity is studied to provide 2-oxazolidinone. It is selected like a modelled reaction in the case of optimizing the reaction factor including the solvent at visible light irradiation utilizing a 32 W CFL. In the present paper, we have found that common heating at solvent-free states is more impressive compared to utilizing organic solvents, with taking into consideration of reaction time as well as production of the desired 2-oxazolidinone (refer to Table 1). The capability to utilize solvent-free states as the reaction zone significantly enhances the green testimonial of the approach.

We have studied the significant pattern of temperature in the production of 2-oxazolidinone at the presence of Ni@ Pd/ZnGlu MNPs that is considered as a catalyst. Outcomes obviously showed that the catalytic activity cannot change temperature of reaction. The most appropriate temperature about this reaction is 25 °C temperature. Higher temperature does not lead to changing the reaction efficiency. The catalyst value essential to enhance the reaction efficiently is tested. It is determined that the changing Ni@Pd/ZnGlu MNP can have significant influence. The most appropriate value of Ni@Pd/ZnGlu MNP was 1.0 mg that acquired the desirable product for 95% production (refer to Fig. 7). At the proper states, the reaction advance in the attendance of an amount of Ni@Pd/ZnGlu MNP (1.0 mg) is analysed using GC. Utilizing this catalyst approach, proper products of 2-oxazolidinone may be obtained during 2 h (refer to Fig. 8). No clear by-products are detected utilizing GC apparatus in whole the experiments as well as the 2-oxazolidinone is cleanly created by 95% production. Influences of carbon dioxide pressure in the attendance of propargylic amine and MNP of Ni@Pd/ZnGlu under the temperature of 25 °C at





Fig. 8 Effect of time on yield of 2-oxazolidinone

Fig. 9 Effect of pressure on yield of 2-oxazolidinone

Table 2 Effect of visible fight intensity of course of the reaction	Table 2	Effect	of visible	light	intensity of	on course	of the	reaction
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Entry	Visible light intensity (W)	Yield (%)
1	_	_
2	8	69
3	15	95
4	20	95
5	22	95
6	32	95

Reaction conditions: propargylic amine (1 mmol), CO_2 1.5 MPa, and Ni@Pd/ZnGlu MNPs (1 mg) under visible light irradiation at room temperature under solvent-free conditions for 2 h

^aIsolated yields

2 h (refer to Fig. 9). The catalyst compound attains an mean conversion more than 95% under pressure of 1.5 Mpa.

In the present paper, a set of experiments is performed by utilizing light of distinct intensities to detect the optimized visible light intensity required to this reaction. In addition, the activity is indicated that when Ni@Pd/ZnGlu MNP is utilized like a catalyst without considering the visible light radiation (refer to Table 2, entries 1). It is showed that the product is identical while 15 W CFL is utilized. Nevertheless, while CFL's of lower intensities are utilized, marginal reduce in production and reaction rate is detected (refer to Table 2, entries 2). Utilizing a CFL of higher wattage upon the other hand not possess any sensible influence on production or time of reaction.

To more investigation of the performance of the catalyst, various control experiments are done and the achieved

Table 3 Comparison of the catalytic efficiency of Ni@Pd/ZnGlu MNPs with various catalysts

1 ZnGlu – 2 Ni@Pd/ZnGlu 95	
2 Ni@Pd/ZnGlu 95	
3 Pd/ZnGlu 95	
4 Ni/ZnGlu 16	
5 Cu/ZnGlu 83	
6 Au/ZnGlu 87	
7 Ag/ZnGlu 78	
8 ZnO/ZnGlu 66	
9 RuO ₂ /ZnGlu 57	
10 TiO ₂ /ZnGlu 50	
11 Pt/ZnGlu 61	
12 FeNi ₃ /ZnGlu 34	

Reaction condition: propargylic amine derivatives (1 mmol), Ni@Pd/ ZnGlu MNPs (1.0 mg), and CO_2 1.5 MPa, under solvent-free conditions and visible light irradiation at room temperature under solventfree conditions after 2 h

^aIsolated yield

information is presented in Table 3. In the first step, one separated reaction is tested at the attendance of ZnGlu. The outcome of this works proved that any value of the proper yield is not created (refer to Table 3, entries 1). According to this disappoint outcomes, we conduct another study to enhance the product ion by adding the NPs in catalyst. NPs that acts as a cocatalyst is known as a essential compound for activating propargylic amines enhancing their catalytic functions. The catalytic behavior of these distinct NPs is determined to be of the discipline Pd ~ Ni@Pd > Au > Cu > Ag > ZnO > Pt > RuO₂ > TiO₂ > FeNi₃ > Ni. As a result, Ni@Pd/ZnGlu MNPs was used in the subsequent investigations because of its high reactivity, high selectivity and easy separation by simple magnet.

The carboxylative cyclization in the case of a diversity of propargylic amines is after wards chosen for exploring the scope of this expanded Ni@Pd/ZnGlu MNP catalytic method. As can be observed in Table 4, aromatic as well as aliphatic propargylic amines done smoothly for giving the relating 2-oxazolidinones in great products.

In comparison to previously reported methods, our method was milder, greener from viewpoint for propargylic amines cyclization with carbon dioxide, support, and metal and costly effective with higher conversion and selectivity towards production of 2-oxazolidinones [53–55]. This comparison clearly exhibits that how powerful our proposed catalyst plays the role of catalyst. It should be noted that in our research, unlike most other reports, a simple nano-metal is used instead of a metal complex. This makes it easy to separate of catalyst from the reaction mixture and reuse it (Table 5).

The reusability state of a catalyst is known as a significant property in the case of the green chemistry. Hence, reusability state MNPs of the Ni@Pd/ZnGlu MNP is

Entry	R ₁	R ₂	R ₃	Product	Yield (%) ^b
1	Н	Н	CH ₃ CH- ₂ CH ₂ CH ₂	2a	88
2	Н	Н	CH ₃	2b	92
3	CH ₃	ΙH	CH ₃	2c	85
4	CH ₃	Н	C ₆ H ₅ CH ₂	2d	91
5	CH ₃	Н	(CH ₃) ₂ CH	2e	90
6	C ₆ H ₅	Н	CH ₃	2f	94
7	$4-CH_3C_6H_4$	Н	CH ₃	2 g	97
8	C_6H_5	CH ₃ CH ₂	CH ₃ CH- ₂ CH ₂ CH ₂	2 h	91

Reaction condition: propargylic amine derivatives (1 mmol), Ni@Pd/ ZnGlu MNPs (1.0 mg), and CO_2 1.5 MPa, under solvent-free conditions and visible light irradiation at room temperature after 2 h

^aYield refers to isolated product

Table 5 An overview of somemethods for synthesis of2-oxazolidinone

Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)	Ref
1	PtCl ₂	DMSO/H ₂ O	60	240	69	[53]
2	CuI	DMSO/H ₂ O	60	120	63	[53]
3	Cu(OAc) ₂	DMSO/H ₂ O	60	114	78	[53]
4	AgOAc	DMSO/H ₂ O	60	24	86	[53]
5	AgOAc	DMSO	60	18	90	[53]
5	Ag ₂ O	DMSO	60	16	92	[53]
7	AgNO ₃	DMSO	60	17	95	[53]
8	AuCl	CH ₃ OH	40	15	0	[54]
9	AuCl(IPr)	CH ₃ OH	40	15	91	[54]
10	AuCl(IMes)	CH ₃ OH	40	15	89	[54]
11	AuCl(ItBu)	CH ₃ OH	40	15	83	[54]
12	$AuCl[P(C_6H_5)_3]$	CH ₃ OH	40	15	41	[54]
13	$AuCl[P(OC_2H_5)_3]$	CH ₃ OH	40	15	61	[54]
14	$AuCl[P(C_2H_5)_3]$	CH ₃ OH	40	15	70	[54]
15	AuBr(IPr)	CH ₃ OH	40	15	84	[54]
16	AuI(IPr)	CH ₃ OH	40	15	71	[54]
17	AgCl(IPr)	CH ₃ OH	40	15	52	[54]
18	CuCl(IPr)	CH ₃ OH	40	15	19	[54]
19	I ^t Bu–CO ₂	CH ₃ OH	40	15	0	[54]
20	AuCl(IPr)	2-Propanol	40	15	55	[54]
21	AgCl(IPr)	CH ₃ CN	40	15	15	[54]
22	AgCl(IPr)	THF	40	15	0	[54]
23	AgCl(IPr)	CH_2Cl_2	40	15	0	[54]
24	AgCl(IPr)	Toluene	40	15	0	[54]
25	ItBu	iPrOH	110	24	89	[54]
26	$({}^{n}C_{7}H_{15})_{4}NBr$	EtOH	60	20	0	[55]
27	$K_8[\alpha$ -Si $W_{11}O_{39}]$	EtOH	60	20	0	[55]
28	K ₆ [SiW ₁₁ O ₃₉ Cu]	EtOH	60	20	43	[55]
29	CuCl ₂	EtOH	60	20	67	[55]
30	$CuCl_2 + ({}^{n}C_7H_{15})_4NBr$	EtOH	60	20	68	[55]
31	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha - SiW_{11}O_{39}Cu]$	EtOH	60	20	95	[55]
32	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha-SiW_{11}O_{39}Co]$	EtOH	60	20	66	[55]
33	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha - SiW_{11}O_{39}Fe]$	EtOH	60	20	18	[55]
34	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha - SiW_{11}O_{39}Ni]$	EtOH	60	20	16	[55]
35	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha-SiW_{11}O_{39}Zn]$	EtOH	60	20	45	[55]
36	$[({}^{n}C_{7}H_{15})_{4} N]_{6}[\alpha - SiW_{11}O_{39}Mn]$	EtOH	60	20	43	[55]
37	SiO ₂ -(CH ₂) ₃ -NEt ₂	_	90	21	72	[13]
38	SiO ₂ –TBD	_	90	21	88	[13]
39	Hydrotalcite MG30	_	90	21	67	[13]
40	Hydrotalcite MG70	_	90	21	58	[13]
41	Al ₂ O ₃	_	90	21	85	[13]
42	Ni@Pd/ZnGlu MNPs	Solvent-free	r.t	2	95	-

investigated at optimal states for synthesis of 2-oxazolidinones. After performing the reaction, the solid MNPs of Ni@Pd/ZnGlu are directly separated from the liquid reaction zone, magnetically, as while nearing a magnet, the solid readily separates from the solution under a few seconds. After solvent cleaning, it may quickly be reused. Figure 10 indicated that the catalyst is reused for tenth consecutive runs. Synthesis of 2-oxazolidinone obtained 92% at the ten run that means only a 3% drop in performance is seen in comparison to the related fresh catalyst (95%). In addition, the value of Palladium leached within the solution for synthesis of 2-oxazolidinone after each run is evaluated using ICP. The catalyst indicated very little leaching in each turn that 0.4% metal leaching discovered



Fig. 10 The reusability of catalysts for synthesis of 2-oxazolidinones

after the ten run, so showing its consistency at the reaction states as illustrated in Fig. 11.

In addition, a complete study is performed to clarify the catalyst heterogeneous nature. Firstly, we done the hot filtration experiment for synthesis of 2-oxazolidinones at premium states and determined that the catalyst is magnetically deleted in situ after 64% for 1 h removal. In addition, the reactants are permissible to tolerate more reaction. The outcomes demonstrated that, after removing the heterogeneous catalyst, the free catalyst remnant is feeble active, and the conversion about 66% is obtained after 2 h of the synthesis of 2-oxazolidinones. It proved that the catalyst worked heterogeneously during the reaction and resentful just slight leaching done in the reaction. Secondly, for ensuring the heterogeneous pattern of the catalyst, the mercury poisoning examine is additionally performed. Mercury (0) is imbibed as a metal or using synthesis and dramatically deactivated the metal catalyst on active surface and so tranquilized the catalyst activity. Conducted experiment is proof of the heterogeneous catalyst. This test has been performed with the aforesaid model of reaction under optimal states. After 1 h of the reaction, about 300 molar mercury is released to the reaction compound. The reaction zone is stirred for above 2 h. In this reaction, no further conversion is seen after 2 h from the catalyst being poisoned. A kinetics scheme of the reaction under the attendance of Hg(0) is demonstrated in Fig. 12. The negative outcomes obtained from the whole heterogeneity experiments (Hg(0) poisoning as well as hot filtration) proposed that the solid catalyst is really heterogeneous and no acquirable Palladium leaching performed upon synthesis of 2-oxazolidinones.

Eventually, for ensuring whether the structure of the recovered catalyst is maintained, we have investigated after the passage of the 10th in the case of photocatalytic synthesis of 2-oxazolidinones at the determined premium states using some investigation as seen in Fig. 13. XPS pattern demonstrated that the Pd elements show in the catalyst fatigued entire after passage of the 10th run then their oxidation condition was same to the fresh catalyst. As seen in Fig. 13a, no other oxidation conditions are detected in the catalyst. As seen in Fig. 13b XRD, pattern of the reproduced catalyst proved that the catalyst structure fatigued totally intact within recycling. The recovered catalyst guaranteed to the outside magnetic zone and can be easily prepared by the reaction mixture like as the fresh catalyst (refer to Fig. 13c). Noted that the nanocatalyst has not indicated any morphological variations that is proved by the FE-SEM pictures, which captured from the recovered catalyst (refer to Fig. 13d). The TEM picture indicated that the a black nanoparticle placed on the structure of ZnGlu were Ni@Pd after the 10th run (refer to Fig. 13e).



Fig. 11 Recyclability of the catalyst for synthesis of 2-oxa-zolidinones



100



Fig. 13 a XPS, b XRD, c VSM, d TEM, and e FE-SEM images of the recovered Ni@Pd/ZnGlu MNPs after the tenth run for synthesis of 2-oxazolidinones

4 Conclusions

In the present paper, we expanded a simple that is highly efficient, obvious light activated and Ni@Pd/ZnGlu, green synthetic method in the case of the cyclization of propargylic amines to carbon dioxide for present 2-oxazolidinones. This visible light and Ni@Pd/ZnGlu compound prepares a simple as well as straight path for chemical stabilization of CO₂. The conditions of reaction show a vast area of functional group to tolerance. This procedure shows proper atom economy (the spent Ni@Pd/ZnGlu MNPs) may be recycled and also reused for mediating task. They have to be helpful for understanding the advantageous mixing of the characteristics of homogeneous along with heterogeneous catalysis and also the expansion of simple catalytic methods. However, this expansion is important in the case of ecological and economical conducts and can assist for minimizing the ecology carbon trace.

References

- Honda M, Tamura M, Nakao K, Suzuki K, Nakagawa Y, Tomishige K (2014) ACS Catal 4:1893–1896
- Song QW, Chen WQ, Ma R, Yu A, Li QY, Chang Y, He LN (2015) Chemsuschem 8:821–827
- Vara BA, Struble TJ, Wang W, Dobish MC, Johnston JN (2015) J Am Chem Soc 137:7302–7305
- Darensbourg DJ, Moncada AI, Choi W, Reibenspies JH (2008) J Am Chem Soc 130:6523–6533
- 5. Yoshida M, Hara N, Okuyama S (2000) Chem Commun 36:151–152
- Wesselbaum S, vomStein T, Klankermayer J, Leitner W (2012) Angew Chem Int Ed 51:7499–7502
- 7. He JM, Sun Y, Han B (2013) Angew Chem Int Ed 52:9620-9633
- 8. Tundo P, Selva M (2002) Acc Chem Res 35:706–716
- Honda M, Tamura M, Nakagawa Y, Tomishige K (2014) Catal Sci Technol 4:2830–2845
- 10. Liu AH, Li YN, He LN (2012) Pure Appl Chem 84:581-602
- Tanaka R, Yamashita M, Nozaki K (2009) J Am Chem Soc 131:14168–14169
- 12. Pulla S, Felton CM, Ramidi P, Gartia Y, Ali N, Nasini UB, Ghosh A (2013) J CO2 Util 2:49–57.
- Maggi R, Bertolotti C, Orlandini E, Oro C, Sartori G, Selva M (2007) Tetrahedron Lett 48:2131–2134
- Kayaki Y, Yamamoto M, Suzuki T, Ikariya T (2006) Green Chem 8:1019–1021
- Feroci M, Orsini M, Sotgiu G, Rossi L, Inesi A (2005) J Org Chem 70:7795–7798
- Aurelio L, Brownlee RTC, Hughes AB (2004) Chem Rev 104:5823–5846
- 17. Chung CWY, Toy PH (2004) Tetrahedron Asymmetry 15:387-399
- 18. Mukhtar TA, Wright GD (2005) Chem Rev 105:529-542
- He X, Deng F, Shen T, Yang L, Chen D, Luo J, Luo X, Min X, Wang F (2019) J Colloid Interface Sci 539:223–234
- 20. Suh MP, Park HJ, Prasad TK, Lim DW (2012) Chem. Rev. 112:782-835
- Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, Bae TH, Long JR (2012) Chem Rev 112:724–781
- 22. Yoon M, Srirambalaji R, Kim K (2012) Chem Rev 112:1196–1231
- 23. Cui Y, Yue Y, Qian G, Chen B (2012) Chem Rev 112:1126-1162

- 24. Corma A, Garcia H, Llabres I, Xamena FX (2010) Chem Rev 110:4606–4655
- 25. Wang JL, Wang C, Lin W (2012) ACS Catal 2:2630-2640
- Schröder F, Esken D, Cokoja M, Berg MWE, Lebedev OI, Van Tendeloo G, Walaszek B, Buntkowsky G, Limbach HH, Chaudret B, Fischer RA (2008) J Am Chem Soc 130:6119–6130
- Vaidhyanathan R, Bradshaw D, Rebilly JN, Barrio JP, Gould JA, Berry NG, Rosseinsky MJ (2006) Angew Chem Int Ed 45:6495–6499
- Kathalikkattil AC, Bisht KK, Aliaga-Alcalde N, Suresh E (2011) Cryst Growth Des 11:1631–1641
- Bisht KK, Parmar B, Rachuri Y, Kathalikkattil AC, Suresh E (2015) CrystEngComm 17:5341–5356
- Ingleson MJ, Barrio JP, Bacsa J, Dickinson C, Park H, Rosseinsky MJ (2008) Chem Commun 11:1287–1289
- Kathalikkattil AC, Bisht KK, Subramanian PS, Suresh E (2010) Polyhedron 29:1801–1809
- 32. Qi C, Ye J, Zeng W, Jiang H (2010) Adv Synth Catal 352:1925-1933
- Roshan KR, Kathalikkattil AC, Tharun J, Kim DW, Won YS, Park DW (2014) Dalton Trans 43:2023–2031
- Roshan KR, Jose T, Kim D, Cherian KA, Park DW (2014) Catal Sci Technol 4:963–970
- Tharun J, Roshan KR, Kathalikkattil AC, Kang DH, Ryu HM, Park DW (2014) RSC Adv 4:41266–41270
- Meilikhov M, Yusenko K, Esken D, Turner S, Van Tendeloo G, Fischer RA (2010) Eur J Inorg Chem 24:3701–3714
- 37. Cheon YE, Suh MP (2008) Chem Eur J 14:3961-3967
- 38. Fang Y, Wang E (2013) Nanoscale 5:1843-1848
- de Pedro ZM, Diaz E, Mohedano AF, Casas JA, Rodriguez JJ (2011) Appl Catal B Environ 103:128–135
- 40. Pérez-Lorenzo M (2011) J Phys Chem Lett 3:167–174
- Hildebrand H, Mackenzie K, Kopinke FD (2009) Environ Sci Technol 43:3254–3259
- 42. Esumi K, Isono R, Yoshimura T (2004) Langmuir 20:237-243
- Metin O, Ho SF, Alp C, Can H, Mankin MN, Gultekin MS, Chi M, Sun S (2013) Nano Res 6:10–18
- Abdullaeua Z, Omurzak E, Iwamoto C, Ganapathy HS, Sulaimankulova S, Chen L, Mashimo T (2012) Carbon 50:1776–1785
- 45. Dong Z, Le X, Dong C, Zhang W, Li X, Ma J (2015) Appl Catal B Environ 162:372–380
- 46. Maitya S, Eswaramoorthy M (2016) J Mater Chem A 4:3233-3237
- 47. Lai Q, Zhang C, Holles JH (2016) Appl Catal A: Gen 528:1-13
- Chen H, Zhang S, Zhao Z, Liu M, Zhang Q (2019) Process Chem 31:571–579
- Yuan D, Zhang C, Tang S, Li X, Tang J, Rao Y, Wang Z, Zhang Q (2019) Water Res 163:114861
- 50. Tang S, Li N, Yuan D, Tang J, Li X, Zhang C, Rao Y (2019) Chemosphere 234:658–667
- Shao P, Tian J, Yang F, Duan X, Gao S, Shi W, Luo X, Cui F, Luo S, Wang S (2018) Adv Funct Mater 28:1705295
- Kathalikkattil AC, Babu R, Roshan RK, Lee H, Kim H, Tharun J, Suresh E, Park DW (2015) J Mater Chem A 3:22636–22647
- 53. Yoshida M, Mizuguchi T, Shishido K (2012) Chem Eur J 18:15578–15581
- 54. Hase S, Kayaki Y, Ikariya T (2013) Organometallics 32:5285-5288
- 55. Wang MY, Song QW, Ma R, Xie JN, He LN (2016) Green Chem 18:282–287

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