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PdO nanoparticles supported on triazole functionalized porous triazine polymer as an efficient heterogeneous catalyst for carbonylation of aryl halides

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Email: drasiva@gmail.com; siva. chem@mkuniversity.org A well-defined triazole functionalized porous triazine based polymers act as solid heterogeneous catalyst after incorporating palladium oxide nanoparticles (PdO@TTAS) have been synthesized and thoroughly characterized by various techniques such as, FT-IR, UV-DRS, solid state ¹³C CP-MAS, XPS, powder Xray diffraction, TGA, SEM and TEM analysis has been detailed illustrated. It is important to note that synthesized catalytic performance for carbonylation of aryl halides (X = I, Br) with EDC.HCl (N-(3-dimethylaminopropyl)-N'ethylcarbodiimide hydrochloride), and formic acid was found to be an effective CO source in the presence of triethylamine as a base and DMF as a solvent medium at 80 °C for about 3 hr. The PdO@TTAS catalyst exhibits superior catalytic performance and along with good yield (up to 90%). Moreover, studying the heterogeneity and reusability of the environmentally friendly solid catalyst can be easily separated by simple filtration and then recycled for several times. In this reaction method, we avoided ligand, additive, promoters and CO gas, due to additional problem arise by using gaseous CO, highly toxic greenhouse gases and high pressurized reaction setup.

KEYWORDS

CO insertion, covalent organic framework, formic acid, Pd nanoparticle, solvothermal

1 | INTRODUCTION

Over the past few decades, there has been exponential development in the field of functionalized porous covalent organic frameworks (COFs), these COFs materials have been constructed by purely organic building unit *via* strong covalent bonds,^[1-4] due to their some textural properties and potential in diverse applications such as high specific surface area, high thermal and chemically stable and large micropore volumes with π -columnar structure, cost-effective and modular synthetic procedure to provide a large number of different polymeric architectures. They exhibited large potential applications in many

research fields, such as gas adsorption,^[5] gas storage,^[6] photocatalyst,^[7,8] solarcells,^[9] chemosensing,^[10,11] gas separation,^[12] water purification membranes,^[13] chiral catalyst,^[14] and especially used for heterogeneous catalyst.^[15–19] In addition to that, porous COF materials are not soluble in any other organic or aqueous medium, highly stable in high-boiling solvents. Hence, these COFs materials are applicable to heterogeneous catalytic system. Among several solid supports are used for catalytic reaction. However, the nitrogen containing functionalized materials is an appropriate choice, because of various benefits, including high surface area, functionalization ability, high stability, and large amount of nitrogen

present in the supports, which is beneficial to immobilize a large number of metal binding sites, which is enhancing the high catalytic activity as well as the stability of the supported materials.

Recently, metal oxide nanoparticles (NPs) have been great attention for current research field and enhance the catalytic activity in heterogeneous catalysis compared with metal nanoparticles, due to their high catalytic properties and some potential applications, these metal oxides nanomaterials have totally differ from bulk metal one, there exists some previously reported literature evidence showed that PdO nanoparticles have high catalytic performance compared to Pd metallic nanoparticles. The heterogeneous PdO nanoparticles was performed to the reduction of 4-nitrophenol,^[20] Pd/PdO NPs supported on carbon nanotubes are utilized to highly efficient catalyst for promoting Suzuki-Miyaura coupling reaction in water medium,^[21,22] Pd/PdO supported on porous graphene as electrocatalyst for methanol oxidation,^[23] and Co₃O₄ nanosheet supported PdO/CeO₂ catalysts are used for methane combustion reactions.^[24] In addition to that, the PdO nanoparticles supported on functionalized polymeric materials act as heterogeneous catalysts shows good catalytic activity and stability than that of commercial available Pd/C catalyst and PdO catalyst can enhance high catalytic activity.

The functionalized covalent organic polymer have been normally used as a metal nanoparticle supports for the dispersion and stabilization of metal nanoparticles due to high surface energy of free nanoparticles tend to aggregate, unique physical properties, inherent size. It shows some selectivity trouble to catalytic reaction without solid supports. Hence we can choose the triazole functionalized polymeric materials will act as good solid supports high surface area and high amount of nitrogen atom present in the polymeric networks.

Generally, aromatic aldehydes are structural motifs present in agrochemicals, many natural products and pharmaceuticals. Transition metal-catalysed carbonylative reactions have been focused extensive research in laboratory-scale, organic synthesis, including industrial processes and medicinal applications.^[25] Although, insertion of carbon monoxide gas into an organic molecule (known as carbonylation), it's a convenient but under developed synthetic route to a number of common functional groups including amides, esters, acids, lactams and lactones.^[26-28] This types of carbonylation reactions are usually carried out at high pressures using carbon monoxide gas in the presence of a palladium-phosphine catalyst, expensive ligands (X-Phos, P-Phos, Phanephos and Bophoz) and can take many hours to completion of the reactions (Scheme 1). Despite considerable success, the major drawbacks associated with such phosphines are environment pollutions and their handling problems, inherent toxicity, difficulty in handling toxic gaseous carbon monoxide, including its storage and transport, represents real problems. Unfortunately, such a disadvantage reduces the overall utility of carbonylation. Furthermore, the alternative formylation reagent like POCl₃/DMF (Vilsmeier-Haack reaction) leads to formation of more reactive iminium adduct. these reagents are widely used for synthetic organic



SCHEME 1 Palladium-catalyzed carbonylative coupling reactions

chemistry, especially the formylation of electron rich aromatics and olefins. However, these reagents are more reactive and hazards. stoichiometric ratio substrate/reagent (1:10), it's difficult to handle and large amount of hydrochloric acid generated from POCl₃, to avoid the above difficulties and replace the direct use of CO gas. In this respect, alternative CO sources have been developed such as amovistannanes,^[29] transition carbonylcomplexes,^[30] N-formylsaccharin,^[31] metal oxalyl chloride,^[32] and carbamoylsilane.^[33] Recently, Xiao-Feng Wu et al. reported the selective synthesis of aldehydes and acids from aryl halides, formic acid as a CO source in the presence of palladium catalysed and ligands controlled.^[34,35] Mohammad Mahdavi et al. also reported the use of Mo (CO)₆ as a solid CO precursor in the Pd supported catalyzed gas-free carbonylationcyclization of N-(2-bromoaryl)benzimidamides reactions has been reported. Furthermore, some of the research groups have been reported for carbonylation reaction using Pd (OAc)₂ homogeneous catalyst and high cost phosphine ligands were shown in comparison Table 4, The homogeneous catalyst totally differ from heterogeneous catalyst, the homogeneous catalyst exhibits highly soluble in solution phase and better activity, high selectivity compared to the heterogeneous catalyst, these types of catalysts and costly ligands have some practical issues like recyclability and catalyst separation, deactivation via aggregation into Pd nanoparticles and also phosphine based ligands are highly toxic, hazards nature in the environment pollutions. In this regards, we have been developed phosphine ligand free and metal nanoparticles stabilized by melamine based solid supports, hazards free, nontoxic, easily degradable for melamine based solid supports, highly stable and insoluble in organic/aqueous media, then effectively utilized to environmental friendly heterogeneous catalysis applications.

In this present work, we wish to report our new achievement on this original idea, to synthesize triazole functionalized covalent organic triazine polymer may immobilized a large number of PdO nanoparticles and robust stability as an efficient heterogeneous catalyst for carbonylation of aryl halides (X = I, Br) using EDC.HCl (N-(3dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) and formic acid as a CO source in the presence of triethylamine and DMF solvent medium at 80 °C for about 3 hr. In this method EDC/HCl and HCOOH used as CO source for the synthesis of desired product, which exhibits high catalytic activity and excellent to good yield (up to 90%). To the best of our knowledge, there is no report describing the carbonylative of aryl halide using HCOOH/EDC.HCl and tiny amounts of PdO@TTAS (15 mg) heterogeneous catalytic systems. The reaction scheme is presented in Scheme 2.

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2 | RESULTS AND DISCUSSION

2.1 | Characterization of TTAS and PdO@TTAS

A new triazole functionalized nitrogen containing TTA (amine-formaldehyde polymer), TTAS (triazole functionalized polymer) and PdO@TTAS (PdO supported on triazole functionalized polymers) was synthesized under solvothermal conditions by condensation reaction between 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline and formaldehyde, PEG/DMF (1:1) solvent in the presence of 1 N NaOH at 140 °C for about 48 hr to obtain triazine based polymeric supported materials (TAS). Furthermore, the synthesized TAS were functionalized with the triazole unit by using n-bromoprop-1-yne and sodium azide in the presence of triethylamine to obtained TTAS material, After that, PdO-NPs successfully incorporated into the TTAS polymeric materials (PdO@TTAS).

The FT-IR spectra of compound PdO@TTAS and corresponding intermediates are shown in Figure 1. The absorption peak that occurs at 2890 cm^{-1} for all the three corresponding materials TTA, TTAS and PdO@TTAS are attributed to the aliphatic C-H stretching frequency band originating from methylene linkers between the two aromatic amine units, respectively. Furthermore, TTAS and TTA contains secondary amine and 1,2,3-triazole N-H stretching band observed at 3355 cm⁻¹ and 3341 cm⁻¹ respectively, based on this observed results, we suggested that formaldehyde was successfully coupled with starting material 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline to provide triazole functionalized TTAS covalent organic polymeric materials. On the other hand, the weak absorption band appeared at 2022 cm⁻¹, 2209 cm⁻¹ for PdO@TTAS and TTAS, which is corresponding to N=N=N- stretching bonds and acetylene C-H stretching frequency. It's strongly suggested that triazole ring successfully functionalized into polymeric network. In addition to that, remaining all the stretching bands are similar pattern observed and hence for all polymeric materials does not show any changes in absorption position, it is clearly represented that structural regularity is well maintained after the synthesis of 1,2,3-triazole functionalized and incorporating Pd NPs.^[43] Finally, the appearance of PdO nanopartical was confirmed by PdO@TTAS absorbance peaks appeared at 521 and 594 cm⁻¹ are attributed to stretching vibrations of PdO nanoparticles.^[44]

The electronic spectra of TTAS and PdO@TTAS were recorded in the range of 200–800 nm shown in (Figure 2). It's provided further evidence for the presence of PdO on polymeric supports. The TTAS and PdO@TTAS both materials show three absorbance band



SCHEME 2 Synthesis of PdO-NPs supported on 1,2,3-triazole functionalized porous triazine polymer networks (PdO@TTAS)



FIGURE 1 FT-IR spectra of compound TTA, TTAS and PdO@TTAS

appeared at 236, 310 and 400 nm, respectively. Which corresponds to π - π ^{*}, n- π ^{*} transition of aromatic phenyl moieties (C=C), core triazine (C=N), and ligand to metal charge transition between metal and imine nitrogen,



FIGURE 2 UV-Diffused reflectance spectra of compound TTAS and PdO@TTAS

respectively. In addition to that, the PdO@TTAS shows all types of transition bands were presented compared with TTAS, which indicates the structural regularity was well maintained after the synthesis of PdO NPs incorporated into the TTAS polymeric materials. Furthermore, PdO@TTAS exhibited a broad absorbance band at range of 500–800 nm due to the charge-transfer transitions of an electron excited from the triazole and triazine nitrogen lone pair to a vacant d-orbitals of the metallic nanoparticles.^[45] It's confirmed that PdO-NPs successfully incorporated into the triazole functionalized polymeric supports.

The X-rays diffraction measurement was used to determine the crystalline structure of synthesized polymeric material, the powder X-ray diffraction (PXRD) pattern of TTA, TTAS and PdO@TTAS shows several peaks over a wide diffraction peak at around the 2θ values 5.4° - 10.7° and 15.3°-26.8° (Figure 3), the set of the broad peak suggested that synthesized covalent triazole polymer (CTPs) materials (TTAS) amorphous nature and higher degree of long range order. Further, the TTAS and PdO@TTAS both materials are compared with TTA, similar pattern and sharp new peaks was observed at around 2θ values 26.66°, 29.67° and 36.19° respectively, which indicates that TTAS was well maintained after the synthesis of PdO@TTAS. It's also confirmed by UV-diffused reflectance spectra. Furthermore, the newly prepared PdO@TTAS polymeric materials having strong diffraction peaks at around 2θ values 40.02° , 46.45° and 67.8° , it can be attributed to the lattice planes of (111), (200) and (220), respectively, which indicating that the well dispersion of PdO nanoparticles for face centered cubic (fcc) lattice arrangement and palladium present in the Pd²⁺ state, which consists with pervious reported literature.^[46,47]

Thermal stability of triazole functionalized covalent triazine polymeric material TTAS and PdO@TTAS has been investigated *via* TGA from 30 °C to 800 °C at 10 °C/min shown in Figure 4, thermal decomposition of TTAS shows two distinct weight loss steps in the temperature range 35– 324 °C and 324–660 °C. The first 4% of weight loss observed



FIGURE 3 Powder X-ray analysis of compound TTA, TTAS and PdO@TTAS



FIGURE 4 Thermogravimetric analysis of compound TTA, TTAS and PdO@TTAS

at 65 °C, which may be assigned to volatilization and vaporization of solvent/small molecules and the second 29% of weight loss observed at 250 °C which corresponds to decomposition of starting material 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline. In addition to that, the PdO@TTAS shows gradual weight loss takes place in a temperature range of 250–554 °C. From the observed results, it's confirmed that both materials TTAS and PdO@TTAS stable up to 250 °C.

In order to confirm the chemical structure of TTAS was performed by ¹³C solid state NMR spectroscopy (Figure 5). The ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectra of compound TTAS displayed ten resonances peak appeared at 170.44, 151.32, 131.36, 130.57, 126.01, 115.20, 110.40, 61.40, 37.10, 31.88 ppm, the presence of core triazine carbon resonate at 170.44 ppm,^[48] and the signal 151.32 ppm corresponds to triazine amine quaternary carbon, whereas the signal appeared at 131.36, 130.57 and 61.40 ppm which were attributed to the 1,2,3-triazole carbons (-CH) and allyl carbon (CH_2) , thus the clearly demonstrated triazole function was successfully incorporated in to the covalent triazine polymeric (TTAS) networks. Furthermore, the signals appeared at 37.10 ppm aliphatic regions which can be assigned to the methylene carbon. In addition to that, all the aromatic carbon appeared at 126.01, 115.20, 110.40 ppm. Based on the obtained results, it is clearly confirmed that the condensation reaction between the 4,4',4"-(1,3,5-triazine-2,4,6-triyl) trianiline and formaldehyde were successfully polymerized through methylene bridging units.^[45,49]

The surface area and porosity of the PdO@TTAS were measured using N_2 adsorption–desorption isotherm technique at 77 K are shown in Figure 6. The Brunauer–Emmett–Teller (BET) total surface area and total pore volume was calculated to be 112.16 m² g⁻¹ and



FIGURE 5 13C CP-MAS NMR spectrum of compound TTAS

0.185 cm³ g⁻¹ (P/Po = 0.987) respectively, (see SI Figure S6) the pore size distribution was calculated using nonlocal density functional theory (NLDFT), the PdO@TTAS does not get uniform pore size. It shows the different pore size was obtained 0.74, 0.93, 1.21 nm, which can be attributed to the synthesized material does not uniform and

ordered, layered structure and it's a micro porous material.

In order to investigate the chemical structure, composition and element valence state of PdO@TTAS determined by XPS analysis are shown in Figure 7 and 8. The obtained survey scans XPS spectrum of the



FIGURE 6 N2 adsorption (filled symbols) /desorption isotherm (empty symbols) and (b) Pore size distributions of PdO@TTAS



FIGURE 7 X-ray photo electron spectrum of compound PdO@TTAS (a) Pd3d spectrum (b) C1s spectrum

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compound PdO@TTAS catalyst represented in the presence of carbon, oxygen, nitrogen and palladium as the constructing elements. The peak appeared at 337.6 eV, 342.9 eV are ascribe to the binding energy values of Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively the binding energy values separation of 5.3 eV between the $3d_{3/2}$ and $3d_{5/2}$, these binding energy values are matched with pervious reported literature.^[50,51] Which had been proven to



FIGURE 8 X-ray photo electron spectrum of compound PdO@TTAS (a) N1s core level spectrum (b) survey scans spectrum



FIGURE 9 SEM Images of compound (a) TTAS (b) PDO@TTAS

palladium present in the supported material as Pd^{2+} in form of PdO nanoparticles. As shown in Figure 7b, the XPS spectrum of C1s can be de-convoluted into three major peaks at 285.2, 286.9, 288.14 eV, respectively. Which is corresponds to the binding energy of C-C/C-H (Sp²), C-N (Sp²) and C-N (Sp³), these results are clearly indicated that triazine triamine and formaldehyde are thoroughly coupled by methylene bridged units to obtained polymeric structure.^[43,52] Furthermore, the XPS spectrum of N1 s core level (Figure 8a) exhibits three peaks at 399.5, 400.3 and 401.4 eV, respectively. It's attributed to the binding energy of C=N for triazine ring, -N=N-and N-H for triazole ring nitrogen. The N1 s core level clearly shows that triazole was successfully functionalized into the porous triazine polymeric supported materials.^[53,54]

In order to investigate the morphological structure for TTAS and PdO@TTAS were confirmed by SEM (scanning electron microscopy) which are shown in Figure 9 and (see SI Figure S8 & S9). The SEM images of both materials showed direct visualization of porous cross-linked structure with partially crystalline nature. The metal content of PdO@TTAS material was investigated using EDS (Energy dispersive X-ray spectroscopy) and elemental mapping was also confirmed in the presence of C (pink),

N (orange), and O (blue) elements and Pd (green) at different points in the porous triazine covalent organic polymers (Figure 10) (See SI Figure S10).

The morphological structure of polymers and average particle size of metal nanoparticles was determined by using Transmission electron microscopy (TEM) which shown in Figure 11. The TEM image of PdO@TTAS represents porous polymer structure and small black dots were represented PdO NPs uniformly dispersed on TTAS porous covalent triazine polymeric materials. Moreover, the average particle size of dispersed palladium nano particles is around 2.89 nm.

2.2 | Catalytic studies of PdO@TTAS for carbonylation of aryl halides

Initially to check the catalytic activity of heterogeneous catalyst PdO@TTAS for carbonylation of aryl halide reaction was conducted using iodobenzene as a model substrate and formic acids act as CO source in the presence of EDC.HCl, triethylamine and DMF solvent at 80 °C, the results are summarized in Table 1. From the table, we observed that the reaction does not undergo in the presence of TTAS, absence of catalyst PdO@TTAS and



FIGURE 10 Elemental mapping of compound PdO@TTAS, C (pink), O (blue), N (orange), Pd (green)



FIGURE 11 TEM images of compound PdO@TTAS

CO source. In these reactions clearly speculated that Pd was playing a crucial role in the carbonylative reactions (Table 1, entry 1 & 2). The reaction was conducted by various CO sources such as HCOOH/DCC, HCOOH/EDC. HCl, CO gas, HCOOH/Ac₂O, oxalic acid and HCOOH/H2SO4, FeCl3/HCOOH investigated. Among the various CO sources, the HCOOH/EDC.HCl to give the highest amount of 90% yield was observed (Table 1, entry 3), and remaining CO sources gave a moderate yield of benzaldehyde and minor amount of benzoic acid as byproduct observed (Table 1, entries 6, 7, 8,12 and 29), the reaction does not effectively undergoes in the presence of Lewis acid FeCl₃ to get red colour solution was observed and CO gas does not effectively generated. Additionally, no product was obtained for neither additive (EDC.HCl) and nor CO source (HCOOH) investigated (Table 1, entries 4, 5, 9, 10 and 11). Among all the tested solvents, DMF provided to the best solvent (Table 1, entries 16-19). Further, various bases were screened, when triethylamine was applied as a base (Table 1, entry 3) to provide 90% of yield. Other bases, including K₂CO₃, pyridine (Py), and piperidine (Pip) provided the desired

product in lower yields (Table 1, entries 20–22). In addition, the reaction was performed with some hindrance bases DIEPA and DIBACO to obtain moderate amount of yield 64% and 40% (Table 1, entry 26, 27). Furthermore, the carbonylative reaction was also carried out in the presence of some commercially available palladium catalysts such as Pd (PPh₃)₄, PdCl₂, Pd/C, Pd (OAc)₂ and our goup also synthesis palladium catalyst and reported instead of PdO@TTAS, providing moderate yield of 68, 60, 50 and 75% (Table 1, entries 22–24 and Table 3). Finally, the reaction temperatures, catalyst loadings, and the loading of other additives and base were optimized as well, but no significant improvement in the yields could be obtained.

Under optimised reaction conditions, we carried out the various substrate scope using HCOOH/EDC.HCl with various substituted aryl halides (X = I, Br) was studied and the obtained results are listed in Table 2, (entries 1–18). The reaction was conducted with a wide range of substrates containing both electron-withdrawing and donating groups substituted on bromobenzene gave corresponding carbonylation products with excellent yield up to 90% and high turnover number up to 2859 (Table 2, entry 1).

 TABLE 1
 Optimization of PdO@TTAS-Catalyzed formylation of aryl halide with CO source

			Catalyst Solvent			
Entry	Catalyst	Solvent	CO Source	Base	Temp. °C	Yield (%)
1	-	DMF	HCOOH/EDC.HCl	NEt ₃	80	NR
2	TTAS	DMF	HCOOH/EDC.HCl	NEt ₃	80	NR
3	PdO@TTAS	DMF	HCOOH/EDC.HCl	NEt ₃	80	90
4	PdO@TTAS	DMF	НСООН	NEt ₃	80	NR
5	PdO@TTAS	DMF	DCC	NEt ₃	80	NR
6	PdO@TTAS	DMF	CO gas balloon	NEt ₃	80	60
7	PdO@TTAS	DMF	EDC.HCl/DCC	NEt ₃	80	60
8	PdO@TTAS	DMF	HCOOH/Ac ₂ O	NEt ₃	80	75
9	PdO@TTAS	DMF	HCOOH/H ₂ SO ₄	NEt ₃	80	NR
10	PdO@TTAS	DMF	(COOH) ₂	NEt ₃	80	NR
11	PdO@TTAS	DMF	EDC.HCl	NEt ₃	80	NR
12	PdO@TTAS	DMF	AcOH/EDC. HCl	NEt ₃	80	20
13	PdO@TTAS	DMF	HCOOH/EDC.HCl	NEt ₃	60	83
14	PdO@TTAS	DMF	HCOOH/EDC.HCl	NEt ₃	90	86
15	PdO@TTAS	DMF	HCOOH/EDC.HCl	NEt ₃	100	80
16	PdO@TTAS	H ₂ O	HCOOH/EDC.HCl	NEt ₃	80	NR
17	PdO@TTAS	DMSO	HCOOH/EDC.HCl	NEt ₃	80	20
18	PdO@TTAS	THF	HCOOH/EDC.HCl	NEt ₃	80	37
19	PdO@TTAS	МеОН	HCOOH/EDC.HCl	NEt ₃	80	NR
20	PdO@TTAS	DMF	HCOOH/EDC.HCl	Pyr	80	45
21	PdO@TTAS	DMF	HCOOH/EDC.HCl	Pip	80	67
22	PdO@TTAS	DMF	HCOOH/EDC.HCl	K ₂ CO ₃	80	12
23	Pd (OAc) ₂	DMF	HCOOH/EDC.HCl	NEt ₃	80	75
24	PdCl ₂	DMF	HCOOH/EDC.HCl	NEt ₃	80	60
25	Pd (PPh ₃) ₄	DMF	HCOOH/EDC.HCl	NEt ₃	80	68
26	PdO@TTAS	DMF	HCOOH/EDC.HCl	DIEPA	80	64
27	PdO@TTAS	DMF	HCOOH/EDC.HCl	DIBCO	80	40
28	PdO@TTAS	ACN	HCOOH/EDC.HCl	NEt ₃	80	55
29	PdO@TTAS	DMF	FeCl ₃ /HCOOH	NEt ₃	80	12

^aReaction conditions: Aryl halide (1 mmol), HCOOH (3 mmol), EDC.HCl (2 mmol), DMF(2 ml), PdO@TTAS (15 mg), 80 °C, triethylamine (1.2 mmol), 3 h, Isolated yield based on aryl halides.

When substrates with electron-withdrawing moieties, such as $-NO_2$, $-COCH_3$, -F, -CHO and -CN, good to excellent yields of the formylated product were obtained (Table 2. Entries 3, 4, 6, 7 and 12). Electron-donating groups, such as -OMe and -Me gave the corresponding products in good yield (Table 2. entries 2, 5, 9, 16). In addition, the electronic properties of *ortho* and *meta* substituted aryl halide had little influence of products in lower yield compared with para substituents (Table 2, entries 10 and

14), due to steric hindrance between the aryl halide and palladium catalyst. Aryl iodides with bromo substitutions were also tolerated well and provided target products, but a moderate amount of yield was observed in bromo substitution. Further, the NH₂, OH functional groups exhibited very less amount of yields was observed and equal amount of N-phenyl formate byproduct also obtained, due to dehydration coupling reaction between the -NH₂, -OH and formic acid in the presence of EDC.HCl (Table 2, entries

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TABLE 2 PdO@TTAS catalyzed formylation of various aryl halides with CO source HCOOH/EDC.HCl^a

$\begin{array}{c} X \\ \hline \\ X = I, Br \end{array} \xrightarrow{PdO@TTAS} \\ HCOOH, EDC.HCI \\ NEt_3, 80 \ ^{\circ}C \end{array} \end{array} $								
Entry	Aryl halide	Product	Temp. (°C)	Time (h)	Yield (%)	TON		
1		СНО	80	3	90	2859		
2		СНО	80	3	80	2364		
3	CI	СНО	80	3	85	2304		
4	O ₂ N	O ₂ N CHO	80	3	86	2237		
5	MeO	МеО	90	4	76	2095		
6	NC	ИС СНО	80	4	79	2225		
7	F Br	F CHO	80	3	81	2354		
8		ОНССНО	95	3	68	1329		
9 ^b	HO	но	90	3	50	1142		
10 ^c	I NH ₂	CHO NH ₂	100	5	41	1207		
11	O Br	0	80	3	75	2630		
12	H ₃ COC	H ₃ COC	90	3	63	2052		
13	Br	СНО	80	3	70	2656		
14		Сно	80	3	82	2520		
15	Br	CHO	90	4	67	2753		
16	Ph	Ph	80	3	78	1797		
17		онс	95	4	72	1144		
18	Br	СНО	80	3	78	3226		

^aReaction conditions: Aryl halide (1 mmol), HCOOH (3 mmol), EDC.HCl (2 mmol), DMF (2 ml), PdO@TTAS (15 mg), 80 °C, triethylamine (1.2 mmol), 3 hr, Isolated yield based on arylhalides TON = mol products/per mol Pd,

^bPhenyl formate,

^cN-phenyl formate was observed.

TABLE 3 Catalytic efficiency of the different palladium metalsource in the carbonylation of aryl halides reactions^a

Entry	Catalyst	Yield
1	Pd/C	60
2	Pd (OAc) ₂	72
3	Pd (PPh ₃) ₄	45
4	Pd/TATAE	54
5	Pd@TATAM	59
6	PdO@TTAS	90

^aReaction conditions: Aryl halide (1 mmol), HCOOH (3 mmol), EDC.HCl (2 mmol), DMF (2 ml), 80 °C,triethylamine (1.2 mmol), 3 hr, Isolated yield based on aryl halides,

^bour group was previously reported palladium catalyst.

9 and 10). It is worth noting that the hetero aryl halides such as 2-iodothiophene, 2-iodofurfural and 3bromopyridine performed well to afford the corresponding products in good to excellent yields (Table 2, entries 14 and 15), Finally, the 4,4'-diiodobiphenyl derivatives also formylated both sides at 95 °C for about 4 h provide good to excellent yield 72% (Table 2, entries 17).

2.3 | Reusability test

Easy to separation the desired product and reusability of the heterogeneous catalyst are an important one for industrial applications and an advantage of PdO@TTAS is its reusability. The reusability of PdO@TTAS heterogeneous catalyst was carried out carbonylation of aryl halide reaction in 4-iodoanisole with HCOOH/EDC.HCl under the optimal reaction conditions (Figure 12a). The catalyst was recovered by normal filtration using Whatman-40 filter paper. The filtered residual solid catalyst was washed thoroughly with methanol and water to removed starting material and followed by vacuum

TABLE 4 Comparison data for pervious reported literature carbonylation of aryl halide reactions with various CO sources

S. No	Catalyst	Solvent	Ligand	Additive	CO Source	Base	Temp (°C)	Time (hrs)	Yield (%)	Ref
Carbonylation reactions										
1	Pd $(OAc)_2$	Toluene	X-phos	Ac ₂ O	НСООН	NEt ₃	80	12	70	[36]
2	Pd $(PtBu_3)_2$	Toluene	X-phos	DMAP	CO gas	-	150	24	75	[37]
3	Pd $(OAc)_2$	Toluene	DMAP	-	$CHCl_3$	КОН	80	12	85	[35]
4	Pd $(OAc)_2$	DMF	PCy ₃	DCC	НСООН	NEt ₃	80	10	75	[29]
5	Pd $(OAc)_2$	Toluene	X-phos	Ac ₂ O	НСООН	NEt ₃	80	12	87	[38]
6	Pd $(OAc)_2$	DMSO	-	DPPP	CO gas		60	20	89	[39]
7	Pd $(OAc)_2$	Toluene	PCy ₃	DCC	НСООН	-	150	6	88	[40]
8	Pd $(OAc)_2$	DMF	X-phos	KF	NFS	NEt ₃	80	20	83	[41]
9	Pd (PtBu ₃) ₂	ACN	-	-	CO gas	NEtPr	115	24	90	[42]
10	PdO@TTAS	DMF	-	EDC. HCl	НСООН	NEt ₃	80	3	90	Present work



FIGURE 12 (a) Reusability experiment of PdO@TTAS catalyst; (b) Effect of reaction time and the percentage of iodo benzene conversion in PdO@TATAs catalyzed carbonylation reactions and Hot filtration test for PdO@TATAS catalyst



SCHEME 3 Synthesis of substituted aldehyde from carbonylation of aryl halide reactions

drying at 85 °C for 1 hr. Further, the catalyst was reused with a fresh charge of solvent and reactants for the next four sequential recoveries; the minor loss of product yield was steadily decreased after each cycle, in addition to that, the FT-IR and UV-diffused reflectance spectra of reused catalyst didn't show any changes in the stretching bands and absorbance bands compared with fresh PdO@TTAS catalyst. These data clearly speculated that catalyst was well maintained and its structural regularity did n't show any changes during the course of the reactions (See SI Figure S1 and S2), these results indicating that stability and reusability of the PdO@TTAS heterogeneous catalyst.

2.4 | Hot filtration test

Finally, the leaching experiment of PdO@TTAS heterogeneous catalyst was investigated by hot filtration test for



SCHEME 4 Plausible mechanism for carbonylation of arylhalides catalyzed by PdO@TTAS

carbonylation of arylhalides, 4-iodoanisole as a model substrate. As a Figure 12b shows, when the catalyst was separated from reaction mixture after one and half hour by centrifugation under hot condition, the filtered portion was added to the another reaction vessel and stirred for further one and half hours under same optimized conditions, the conversion of the filtered sample (catalyst filtered) remains practically unchanged, while the unfiltered one that the present in heterogeneous catalyst to increase product conversion. However, Figure 12b also shows that once the reaction solution is filtered, the obtained solution shows there is no significant improvement in the product conversion. These results proved that the PdO@TTAS were stable at the reaction condition and no leaching of PdO NPs in the filtrate solution, it's confirmed that the catalyst is truly heterogeneous in nature.

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2.5 | Proposed mechanism

In order to investigate, the plausible mechanism for carbonylation of arylhalide catalyzed by PdO@TTAS heterogeneous catalyst was proposed in Scheme 3, which consisted with previous reported literature.^[34,38] In the first step the oxidative addition of aryl halide interact with palladium nanoparticles to form the Pd complex II and then followed by insertion of carbon monoxide from *in-situ*

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generated HCOOH/EDC.HCl in the presence of triethylamine to generate *in-situ* CO gas.

After that, CO gas interact with metal to form M- π interaction (complex III), and then followed by CO migration occurred (complex IV), next step formic acid coordinated to the η^3 -bonding mono dentate ligand (complex V) and followed by decarboxylation, the reductive elimination reaction was occurred to obtain expected desired product. Further, the catalyst PdO@TTAS was successfully continued to further consecutive cycles. Furthermore, from the comparison data for pervious reported literature carbonylation of aryl halide reactions with various CO sources and different palladium catalyst, ligands, additives are summarized in Table 4.

3 | CONCLUSIONS

In conclusion, we have designed, synthesis of PdO NPs supported on triazole functionalized triazine containing covalent organic polymer (PdO@TTAS). The catalytic activity of PdO@TTAS to carry out the carbonylation of aryl halides with formic acid as a CO source, highly desirable, environmentally acceptable reagents, economically viable and hazardous free, although it has to activate by a sacrificial material, such as EDC.HCl. In addition, the reaction was carried out without any additional stabilizing agents such as ligands, additives and also we got very good to excellent yield over a very short reaction time. The reaction system shows tolerance toward numerous substituted aryl halide to obtain the desired products in good yield, there is no reports describing to generate CO gas with the help of HCOOH/EDC. HCl into the carbonylation of aryl halides. Furthermore, the catalyst PdO@TTAS represents a very good reusability results, and without significant loss of the catalytic activity also observed after five sequential runs. Hence, the reactions employing environmentally friendly solvent and no additives/inert atmosphere/ligand free protocol.

4 | EXPERIMENTAL SECTIONS

4.1 | Materials and methods

All the chemicals and reagents were purchased from commercial reagent suppliers, used without further purification as commercially available unless otherwise noted. All the solvents were obtained from laboratory reagent grade. The ¹H and ¹³C NMR spectra were recorded on a Bruker (Avance) 300 and 400 MHz NMR instrument using TMS as an internal standard and CDCl₃ as a solvent. Chemical shifts are given in ppm (δ -scale) and the coupling constants are given in Hz. UV-Diffused

reflectance spectra was recorded using JASCO-500. ¹³C CP-MAS NMR was recorded using a Bruker Avance 500 MHz operating at 75 MHz for ¹³C nuclei. The FT-IR spectra were recorded from a JASCO FT/IR-410 spectrometer. The thermal stability of the samples was evaluated by TGA (SCINCO thermal gravimeter S-1000, Japan) under the Argon (Ar) atmosphere over the temperature range up to 30-800 °C, in flowing argon gas at the heating rate of 10 °C min⁻¹. The surface area of the samples was calculated by using the Brunauer-Emmett-Teller (BET) method and the pore sizes of the samples were calculated using the NL-DFT model. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku diffractometer using CuK α ($\lambda = 1.5404$ Å) source with a scan rate of 0.5° min⁻¹. The N₂ adsorption-desorption isotherms were measured on a BELsorp-Max (BEL, Japan) at 77 K. The morphology and particle size of the polymerized materials were examined by SEM and TEM. The scanning electron microscopy (SEM) measurements were performed by VEGA3 TESCAN, Czech Republic. The Energy dispersive X-ray spectroscopy (EDX) was carried out using Bruker Nano, Germany. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of n-hexanes and ethyl acetate as an eluent. Column chromatography was carried out on silica gel (60-120 mesh) using nhexanes and ethyl acetate as an eluent.

4.2 | Synthesis of 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline

To a stirred solution of 4-aminobenzonitrile (2 g, 16. 92 mmol) was dissolved in a very less amount of CHCl₃ under a nitrogen atmosphere and maintained at 0 °C for about 1 hr. After that trifluoromethanesulfonic acid (CF₃SO₃H) (4 ml) was drop wisely added into the reaction mixture and stirred well, further the reaction mixture was warmed to room temperature and stirred for 8 hr. The resultant light yellow pasty solid was obtained and then crushed ice added into the pasty solid, neutralized with ammonium hydroxide to get a desired light yellow precipitate. Further, the insoluble precipitate was filtered off and washed with water, and then yellow colour powder was dried in vacuum oven at 60 °C to afford 80% of pure product (see SI Figure 12 & 13).

4.3 | Synthesis of TTA polymer

Compound 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (0.65 g, 1.833 mmol) and formaldehyde (40% solution) (0.165 mg, 1.833 mmol) were mixed with polyethylene glycol (PEG-400)/DMF(1:1) solvent taken in a 100 ml

Schlenk tube. The resultant homogeneous solution was treated with a 6 M acetic acid drop wisely added into the reaction mixture and then pH of the solution was adjusted to 10 via added for 1 N NaOH solution. Further, the reaction mixture was carried out under vigorous stirring at 75 °C for about 30 mins and capped tightly, a clear solution was obtained and then Schlenk tube was fitted into the oil bath at 140 °C for about 48 hr. After completion of the reaction, the highly viscous liquid was poured into 100 ml of water and stirred for 2 hr, the light yellow colour solid was completely settled into the bottom of aqueous solution. After that, the solid was filtered and subsequently washed with organic solvents to remove the unreacted starting materials. Then, the solid was immersed in acetone for one day and filtered, dried at 80 °C under the vacuum oven for 6 hr to get 82% yield. FT-IR (powder cm⁻¹) 3355, 2874, 1610, 1510, 1431, 1366, 1182, 1148, 812, 582, 529. Elemental analysis calculated from EDS analysis (Atomic %) for C 79.55, N 13.80, 0 6.59.

4.4 | Synthesis of Triazole functionalized TTAS polymer

The TAS solid supports (1 g, 2.821 mmol) and 3bromoprop-1-yne (1.06 g, 8.910 mmol) was taken in a 100 ml flask and then mixed with DMF/PEG-400 solvent in the presence of triethylamine base (0.856 g, 8.456 mmol), then the reaction mixture was carried out under vigorous stirring at 90 °C for about 3 hr, after that sodium azide (NaN₃) (0.55 g, 8.46 mmol) was added into the reaction mixture and stirred at 120 °C for about 8 hr. The resultant slurry solution was poured into the water and neutralized with dil. HCl to obtain light brown colour solid. Furthermore, the solid was filtered and subsequently washed with organic solvents to remove the unreacted starting materials. After that, the solid was immersed in acetone for one day and filtered, dried at 80 °C under the vacuum oven for about 6 hr to get 80% of yield. FT-IR (powder cm⁻¹) 3349, 2861, 2017, 1669, 1602, 1504, 1431, 1372, 1174, 1142, 80, 588, 516. Elemental analysis calculated from EDS analysis (Atomic %) for C 69.70, N 18.28, O 12.02.

4.5 | Synthesis of Pd@TTAS polymer

To take a $PdCl_2$ (0.05 g) solid metal salt and (0.5 g) of TTAS solid polymeric supports were mixed with 5 ml of MeOH into a 25 ml round bottom flask, the mixture was stirred at room temperature. After that, the concentrated 0.5 ml of hydrochloric acid was added; the $PdCl_2$ was converted into $H_2PdCl_4.H_2O$ and then subsequently

aq. NaoH was added drop-wise with vigorous stirring to adjust the pH of the precursor solution and also maintained constant stirring at 75 °C for about 2 hr. Finally, the colour of the solution was changed into brownish black and triazole functionalized palladium oxide NPs was obtained. The solid PdO@TTAS collected and then filtered through a Whattman 40 filter paper and washed with MeOH (25 ml), DCM (20 ml), acetone (20 ml) and THF (10 ml) to remove the unreacted palladium chloride, then PdO@TTAS heterogeneous catalyst was filtered and dried in a vacuum oven at 70 °C for about 8 hr to obtain PdO@TTAS as a brown colored powder (0.48 g, 87% of yield) (Scheme 2). FT-IR (powder cm^{-1}) 3329, 2867, 2209, 1602, 1498, 1366, 1254, 1182, 1135, 1089, 938, 812, 582, 522. Elemental analysis calculated from SEM-energy dispersive X-ray spectrascopy analysis (Atomic %) for C 67.39, N 21.67, O 9.24, Pd 1.70. The Pd content 1.82% were calculated from inductively coupled plasma-optical emission spectroscopy (ICP-OES).

4.6 | General reaction procedure for carbonylation of aryl halides

The potential catalytic activities of newly synthesized and thoroughly characterized heterogeneous PdO@TTAS catalyst were analyzed by carbonylation of aryl halide reactions. Aryl halides and HCOOH were dissolved in DMF solvent and stirred in a closed Schlenk tube, subsequently added PdO@TTAS catalyst (10 mg) and followed by the addition of EDC.HCl (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hvdrochloride) and triethylamine to obtain brisk effervescence was observed, bubbles of carbon monoxide gas are insitu generated vigorously and the reaction mixture was stirred at 80 °C for about 3 hr. After completion of reaction (monitored by TLC), the mixture was neutralized with dilute NaHCO₃ solution and diluted with 5 ml ethyl acetate, then the catalyst was removed by simple filtration using Whatman-40 filter paper. The filtrate was extracted with excess amount of ethyl acetate, and then concentrated under reduced pressure. The crude product was further purified by column chromatography (petroleum ether/ethyl acetate) to afford the corresponding product (Scheme 4).

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