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Article

Pd@CuMoO₄ Polyoxometalate as an Efficient and New Heterogeneous Catalyst for the Suzuki-Miyaura and Sonogashira-Hagihara Coupling Reactions

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Abstract: This study investigates the preparation, characterization, and catalytic activity of a novel palladium-doped copper molybdate polyoxometalate (Pd@CuMoO₄). Using a mere 19 ppm of palladium, Pd@CuMoO₄ demonstrated excellent yields in both Suzuki-Miyaura and Sonogashira-Hagihara coupling reactions of aryl halides with boronic acids and alkynes, respectively. The synergistic effects between the different metals in this catalyst were confirmed to be responsible for its high catalytic performance. Additionally, Pd@CuMoO₄ was successfully recovered and recycled multiple times in the Suzuki-Miyaura reaction with minimal loss of activity. The structural integrity of the reused catalyst was evaluated through various analytical techniques.

Keywords: Polyoxometalate; Palladium; Suzuki; Sonogashira-Hagihara; synergistic effects

1. Introduction

Synergistic effects arising from the combined action of different metal centers in multimetallic catalysts often result in enhanced efficiency for various organic transformations. Positive cooperativity among metals occurs when the binding of one metal enhances the substrate's affinity for another, likely due to electron sharing within the bi- or multimetallic system. This phenomenon contributes to the unique reactivity observed in both homogeneous and heterogeneous catalysts [1–4].

Homogeneous and heterogeneous catalysts have their own strengths. Heterogeneous catalysts are easily recovered by filtration, enabling product purification and catalyst recycling. However, leaching of the active metal catalyst into the reaction solution can sometimes occur, making the distinction between homogeneous and heterogeneous catalysis less clear [5–7].

Polyoxometalates (POMs) are inorganic polyanions with a well-defined structure, consisting of metal ions linked by oxyanions to form a large, closed framework [9]. Polyoxometalates (POMs) are promising catalysts for various organic transformations due to their unique structure and redox activity. Multi-metallic POMs can offer enhanced catalytic performance compared to monometallic ones. A common preparation method involves depositing one metal onto another, similar to platinum catalysts supported on carbon or alumina. The proximity between metal centers in these materials likely facilitates improved catalytic properties through direct metal-metal interactions [8,10–14].

Copper molybdate (CuMoO₄) is an inorganic compound with valuable applications in catalysis, photocatalysis, and electrochemistry, thanks to the synergistic effects between copper and molybdenum [16,17]. CuMoO₄ is a versatile material with applications in catalysis, photocatalysis, and electrochemistry. Its redox properties and the ability of molybdenum to change oxidation states

contribute to its catalytic efficiency in selective oxidation reactions. CuMoO_4 also exhibits photocatalytic activity for degrading organic pollutants under visible light, and has potential in energy storage systems like lithium-ion batteries due to its conductive properties and capacity for charge storage [15,18].

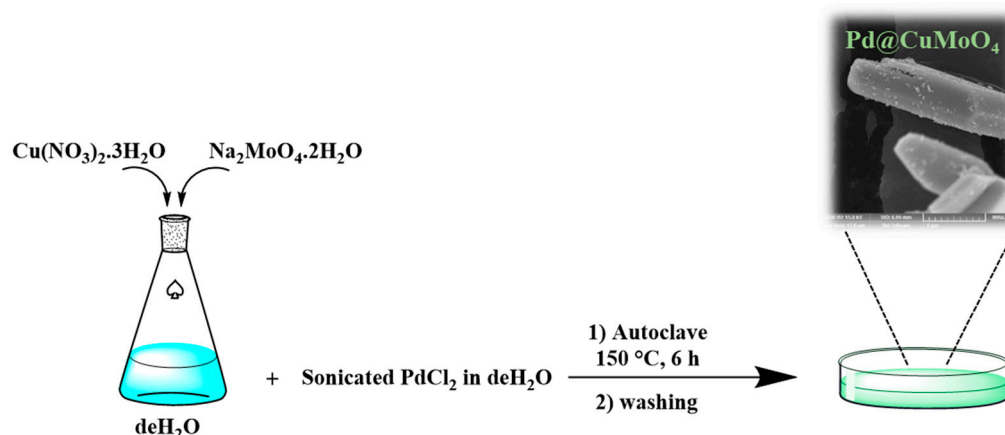
Carbon-Carbon coupling reactions are essential for synthesizing various organic compounds, including pharmaceuticals, agrochemicals, and other valuable molecules. These reactions involve joining two hydrocarbon fragments to form a new carbon-carbon bond. Examples include the Mizoroki-Heck, Suzuki-Miyaura, Sonogashira-Hagihara, Stille, and Negishi reactions [19–22,26].

The Suzuki-Miyaura reaction is a palladium-catalyzed coupling of aryl halides or pseudo halides with organoboron compounds in the presence of a base. This method provides an efficient and clean way to selectively form carbon-carbon bonds [23–25,27]. The Sonogashira-Hagihara reaction is a valuable tool for coupling terminal acetylenes with aryl or vinyl halides, leading to the formation of aryl alkynes and conjugated enynes. These compounds are important building blocks for various products, including pharmaceuticals, agrochemicals, and other materials. The reaction typically uses palladium catalysts with copper(I) co-catalysts, making it a promising candidate for the development of palladium-copper bimetallic nanoparticle catalysts [19,26,28–30].

2. Results and Discussion

2.1. Preparation and Characterization of Pd@CuMoO_4

The steps for preparation of Pd@CuMoO_4 are summarized in Scheme 1.



Scheme 1. Preparation of Pd@CuMoO_4 .

The morphological and physical properties of Pd@CuMoO_4 was studied by different techniques and analyses such as transmission electron microscopy (TEM), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDX), EDX-mapping and X-ray diffraction (XRD).

The XPS of Pd@CuMoO_4 was investigated in the Cu, Mo, and Pd regions. In the XPS spectrum of copper, $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ core-levels are detected because of the minor peaks centered at 932.7 and 952.21 eV, which are related to copper(I), and the peaks observed at 934.4 and 954.3 corresponding to copper(II) species. Peaks located at 941.1, 942.4 and 962.1 eV are satellite peaks [31–34]. XPS in Mo region showed 3d core-levels with a distinct doublet centered at 232.3 and 235.4 eV. The energy difference of this doublet (3.2 eV) and location of peaks confirm oxidation state of Mo^{6+} (Figure 1) [35,36].

XPS of Pd@CuMoO_4 at Pd region confirmed the presence of Pd showing Pd3d core levels which split into $3d_{5/2}$ (located at ~ 337.6 eV) and $3d_{3/2}$ (centered at ~ 342.8 eV). These data perfectly matched with a palladium(II) state [37].

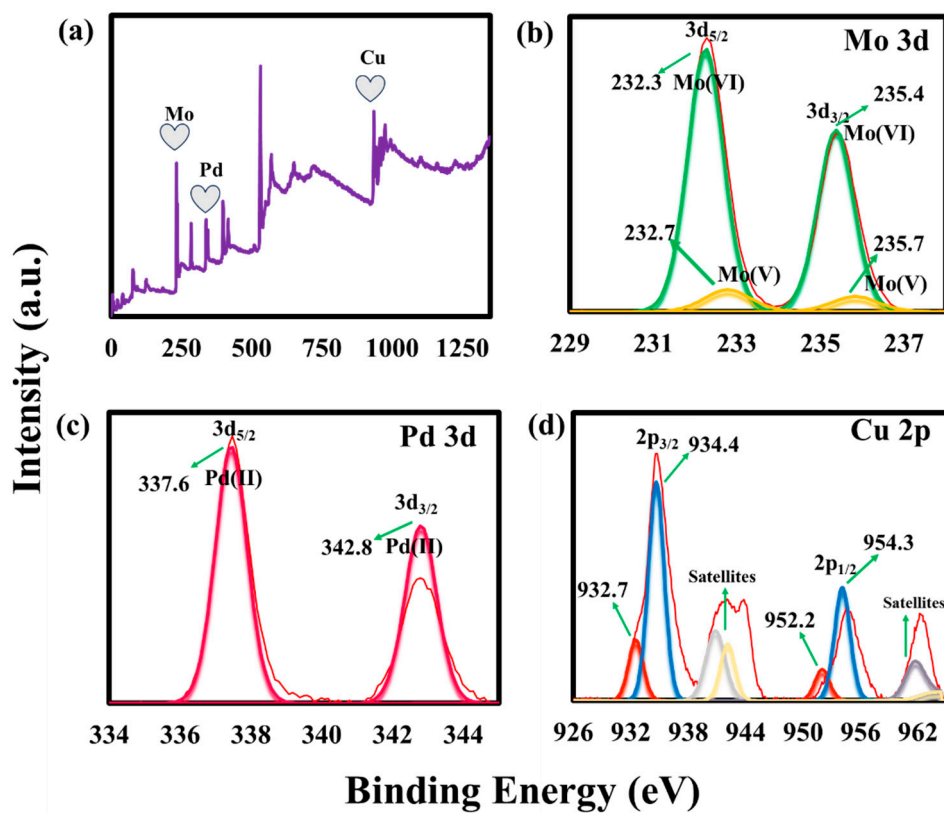


Figure 1. XPS spectrum of Pd@CuMoO₄ catalyst, (a) all elements, (b) Mo 3d, (c) Pd 3d, (d) Cu 2p.

SEM and TEM images of Pd@CuMoO₄, captured at different magnifications, revealed a well-defined rectangular or tetragonal cubic structure, characteristic of the polyoxometalate compound (Figure 2).

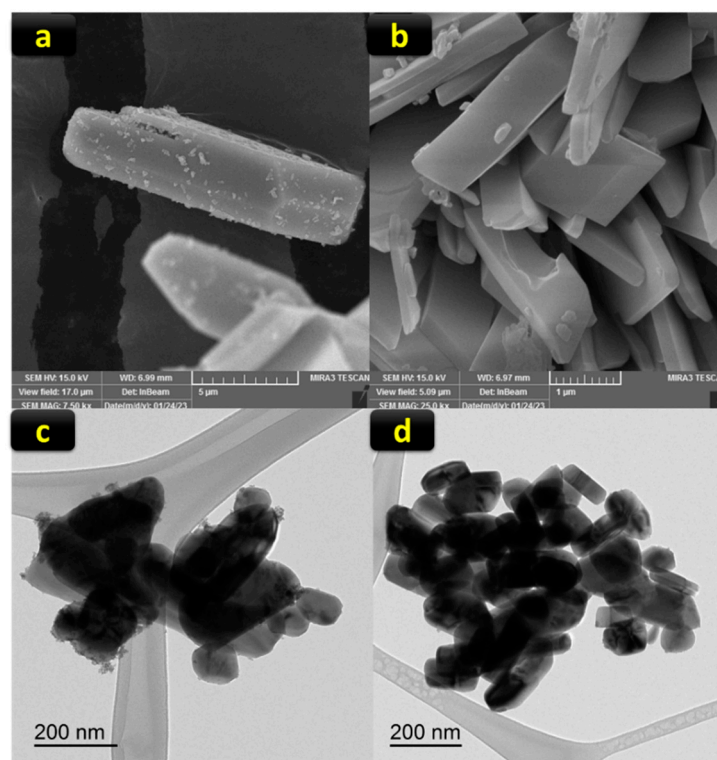


Figure 2. SEM (a and b) and TEM (c and d) images of Pd@CuMoO₄.

The elemental mapping images of Pd@CuMoO₄ confirmed the presence of Pd, Cu, and Mo elements (Figure 3). The existence of these elements was further confirmed by EDX analysis (Figure S1).

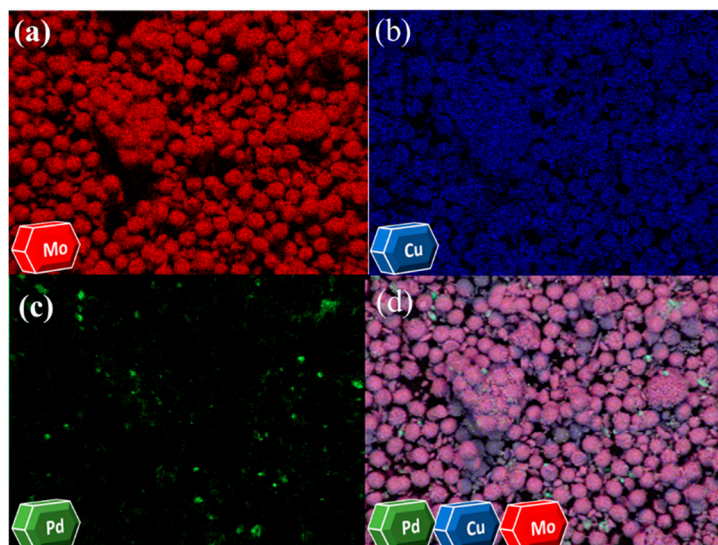


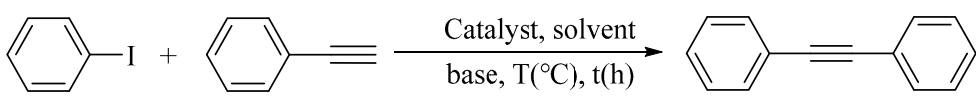
Figure 3. EDX-mapping image of Pd@CuMoO₄.

XRD of Pd@CuMoO₄ was also studied and the obtained results fitted with the reported CuMoO₄ [38,39]. However due to low concentration of palladium and its overlap of its peaks with the signals of CuMoO₄, related peaks to palladium are not detectable (Figure S2).

2.2. Catalytic Performance of Pd@CuMoO₄

The catalytic performance of Pd@CuMoO₄ was initially evaluated in the Sonogashira-Hagihara reaction using iodobenzene as a model substrate. A comprehensive study of various parameters, including solvent, base, catalyst amount, temperature, and reaction duration, was conducted (Table 1). Several Pd@CuMoO₄ loadings in solvents such as polyethylene glycol (PEG), dimethylformamide (DMF), and a 1:1 mixture of EtOH and H₂O produced different efficiencies in this reaction. The results demonstrated that with 10 mg of catalyst and DABCO as a base in DMF at 80 °C, the product was obtained in 96% yield, while at 60 °C the yield decreased to 83% after 24 h (Table 1, entries 1 and 2). However, lowering the temperature to 30 °C the chemical yield was reduced to a 68% (Table 1, entry 3). Increasing the catalytic amount to 15 mg and using DABCO as a base, 97% and 45% yields were obtained during 24 and 12 h, respectively (Table 1, entries 4 and 5). Using other solvents such as PEG 200 and aqueous ethanol or other bases such as K₂CO₃, yields were not improved (Table 1, entries 6-10). Therefore, for the reaction of iodobenzene with phenylacetylene, the highest yield was obtained when DABCO was used as a base, at 60 °C, and 15 mg of Pd@CuMoO₄ in DMF as solvent (containing 19 ppm of Pd). Under similar conditions, CuMoO₄ exhibited poor yield and lower efficiency than the reaction performed with Pd@CuMoO₄ (Table 1, entry 11). Also, using the same amount of homogeneous PdCl₂, a 70% yield of diphenylacetylene was obtained indicating the important role of Pd and CuMoO₄ in the overall catalytic activity (Table 1, entry 12).

Table 1. Optimization of Sonogashira-Hagihara reaction for compound Iodobenzene using Pd@CuMoO₄ catalyst.



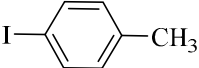
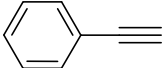
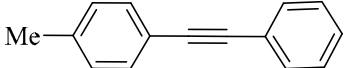
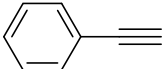
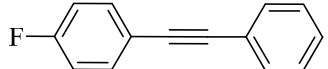
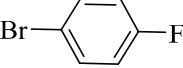
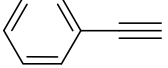
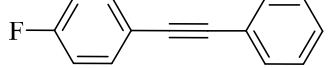
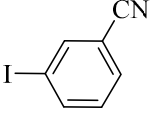
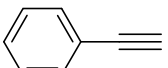
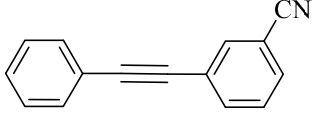
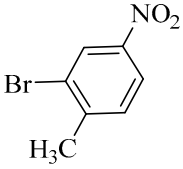
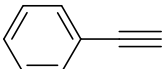
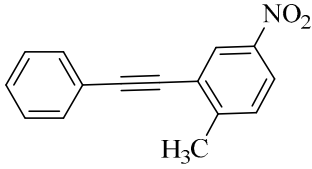
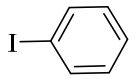
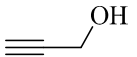
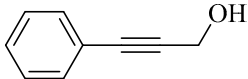
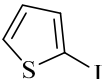
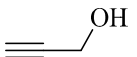
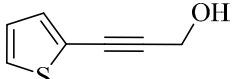
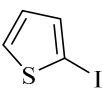
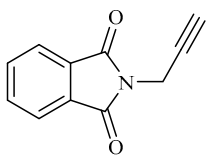
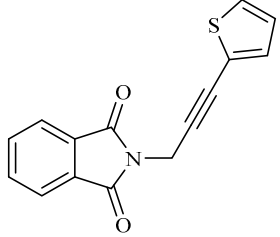
Entry	Catalyst	Amount of catalyst (mg)	base	T (°C)	Solvent	Time (h)	Yield [%]
1	Pd@CuMoO ₄	10	DABCO	80	DMF	24 h	96%
2	Pd@CuMoO ₄	10	DABCO	60	DMF	24 h	83%
3	Pd@CuMoO ₄	10	DABCO	30	DMF	24 h	68%
4	Pd@CuMoO ₄	15	DABCO	60	DMF	24 h	97%
5	Pd@CuMoO ₄	15	DABCO	60	DMF	12 h	45%
6	Pd@CuMoO ₄	15	DABCO	60	PEG	24 h	4%
7	Pd@CuMoO ₄	15	DABCO	60	H ₂ O:EtOH	24 h	4%
8	Pd@CuMoO ₄	15	K ₂ CO ₃	40	DMF	24 h	n.r
9	Pd@CuMoO ₄	15	K ₂ CO ₃	40	H ₂ O:EtOH	24 h	n.r
10	Pd@CuMoO ₄	15	K ₂ CO ₃	60	H ₂ O:EtOH	24 h	5%
11	CuMoO ₄	10	DABCO	80	DMF	24 h	2%
12	PdCl ₂	Same as Cat.	DABCO	60	DMF	24 h	70%

Using the optimized reaction conditions, the Sonogashira-Hagihara reaction was further explored with a broad range of aryl halide derivatives and three different terminal alkynes (Table 2).

The results showed that aryl halides containing electron-donating groups such as CH₃, OH, and OCH₃ as well as with electron-withdrawing groups like F, Cl, Br, I, CN, NO₂, CHO, and COCH₃ gave very good to excellent yields of the desired products. Compounds with iodine as the leaving group facilitated the Sonogashira-Hagihara reactions, owing to iodine's superior leaving power compared to bromine (Table 2). Additionally, the Sonogashira-Hagihara reaction of heterocyclic compounds such as 2-iodothiophene and 5-bromopyrimidine afforded excellent and very good yields, respectively (Table 2, entries 9, 17, 18, and 8). It should be noted that the optimal conditions employed 15 mg of catalyst, 0.3 mmol (33.6 mg) of DABCO as base, and 1.5 mL of DMF as solvent.

Table 2. Sonogashira-Hagihara reaction of aryl halides and three different terminal alkynes catalyzed by Pd@CuMoO₄^[a].

Entry	Ar-X	R'—C≡C—H	Product	Time (h)	Yield [%] ^[a]
1				18	97
2				18	89
3 ^[b]				18	>99
4				24	96
5 ^[c]				18	89
6 ^[c]				18	>99
7 ^[c]				24	86
8 ^[c]				24	80
9				18	>99
10 ^[b]				20	>99

11				22	92
12 ^[b]				20	98
13 ^[c]				24	87
14				18	88
15 ^[c]				24	90
16 ^[c]				24	96
17 ^[c]				20	95
18 ^[c]				18	95

[a] Reaction conditions: Catalyst (15 mg, 19 ppm Pd), DMF (1.5 mL), ArX (0.2 mmol), Alkyne (0.3 mmol), DABCO (0.3 mmol, 33.6 mg) at 60 °C under argon atmosphere. [b] Reactions were performed at 70 °C. [c] Reactions were performed at 80 °C. [d] GC yields.

To expand the catalytic activity of Pd@CuMoO₄, its efficiency in the Suzuki-Miyaura coupling reaction was assessed. To optimize the conditions, 4-bromobenzaldehyde was selected as the model compound and various parameters, such as amount of catalyst, temperature, solvent, and reaction time, were investigated. Conducting the reaction in pure water at 80 °C with 15 mg of catalyst for 24 h, a 23% conversion was achieved (Table 3, entry 1). Increasing the catalyst amount to 20 mg the yield was not ameliorated (Table 3, entry 2). In addition, using EtOH as a solvent the desired product was not satisfactorily obtained (Table 3, entries 3 and 4). Subsequently, a 1:1 mixture of H₂O and EtOH was tested. This solvent combination effectively improved reaction efficiency, leveraging the synergistic properties of both solvents. Polarities and features of water-EtOH mixture created favorable conditions for the solubility of both organic and inorganic reactants, enhancing the reaction rate and yield (Table 3, entry 5). Reducing the catalyst amount resulted in minimal changes in efficiency, suggesting that the catalyst maintains high efficacy even at lower concentrations (Table 3,

Under these optimal conditions, the performance of the Pd@CuMoO₄ catalyst was compared to the CuMoO₄ bimetallic compound in the Suzuki-Miyaura reaction of 4-bromobenzaldehyde with phenylboronic acid. Results indicated that the efficiency of the reaction using CuMoO₄, under identical conditions, was only 5%, and increasing the temperature the yield was not improved (Table 3, entries 12 and 13). Further evaluation by adding palladium salt homogeneously to the reaction medium resulted in a yield of 27%, demonstrating a significant synergistic effect between palladium and CuMoO₄ in the catalyst composition (Table 3, entry 14).

$$\text{Br}-\text{C}_6\text{H}_4-\text{CHO} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{Solvent, T}^\circ\text{C), t(h)}]{\text{Pd@CuMoO}_4, \text{K}_2\text{CO}_3} \text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{CHO}$$

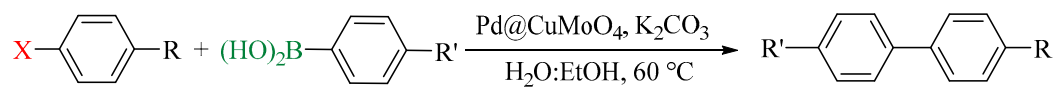
Entry	Catalyst	Amount of catalyst	Solvent	T (°C)	t(h)	Yield [%]
		(mg)				
1	Pd@CuMoO ₄	15	H ₂ O	80	24 h	23%
2	Pd@CuMoO ₄	20	H ₂ O	80	24 h	31%
3	Pd@CuMoO ₄	15	EtOH	60	24 h	25%
4	Pd@CuMoO ₄	20	EtOH	60	24 h	30%
5	Pd@CuMoO ₄	20	H ₂ O:EtOH (1:1)	60	24 h	>99%
6	Pd@CuMoO ₄	15	H ₂ O:EtOH (1:1)	60	24 h	>99%
7	Pd@CuMoO ₄	15	H ₂ O:EtOH (1:1)	60	15 h	>99%

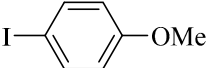
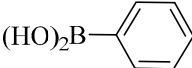
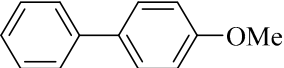
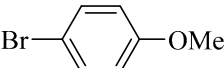
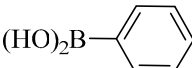
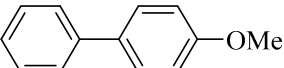
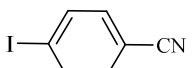
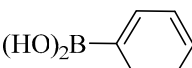
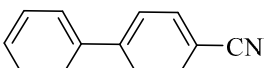
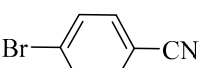
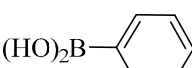
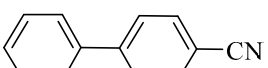
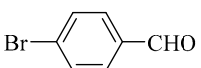
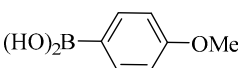
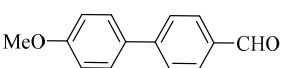
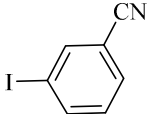
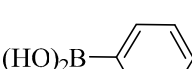
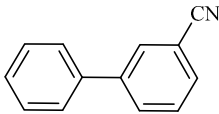
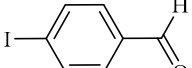
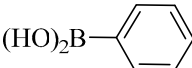
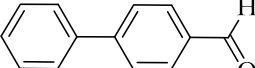
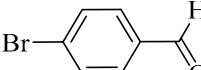
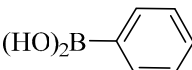
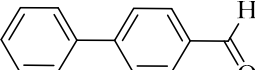
8	Pd@CuMoO ₄	15	H ₂ O:EtOH (1:1)	60	2 h	>99%
9	Pd@CuMoO ₄	15	H ₂ O:EtOH (1:1)	60	1 h	75%
10	Pd@CuMoO ₄	10	H ₂ O:EtOH (1:1)	60	2h	89%
11	Pd@CuMoO ₄	5	H ₂ O:EtOH (1:1)	60	2h	40%
12	CuMoO ₄	15	H ₂ O:EtOH (1:1)	60	24 h	5%
13	CuMoO ₄	20	H ₂ O:EtOH (1:1)	80	24 h	9%
14	PdCl ₂	Same as Cat.	H ₂ O:EtOH (1:1)	60	24 h	27%

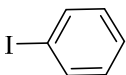
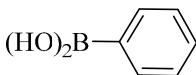
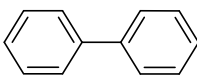
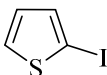
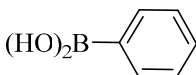
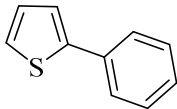
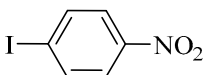
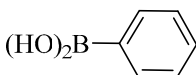
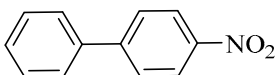
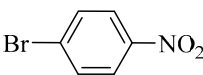
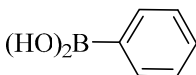
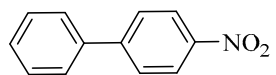
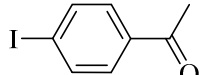
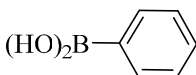
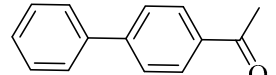
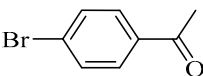
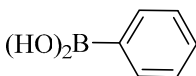
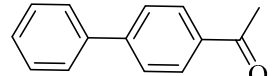
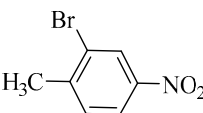
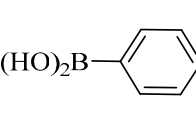
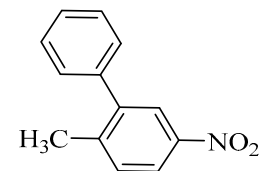
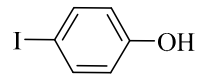
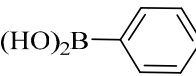
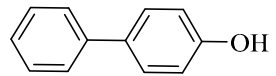
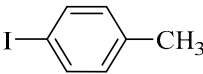
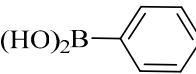
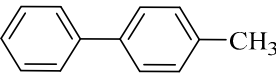
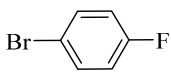
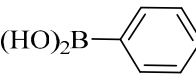
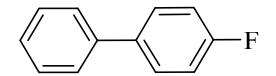
Having established optimal conditions, the Suzuki-Miyaura reaction was explored with a wide range of aryl halides together with aryl boronic acids (Table 4). Aryl halides containing both electron-donating and withdrawing groups were appropriate to run this Suzuki-Miyaura reaction furnishing the corresponding biaryls in very good to excellent yields.

Notably, the Suzuki reaction of the heterocyclic compound 2-iodothiophene was performed efficiently in a short reaction time (Table 4, entry 10). All reactions were conducted under optimal condition at 60 °C using 15 mg of catalyst.

Table 4. The Suzuki-Miyaura cross-coupling reaction of aryl halides with aryl boronic acid using the Pd@CuMoO₄ catalyst^[a].



Entry	Ar-X	Ar'-B(OH) ₂	Product	Time (h)	Yield (%) ^[b]
1				5	98
2				24	75
3				1	93
4				3	91
5				3	93
6				3	97
7				1	>99
8				2	>99

9				3	>99
10				3	98
11				1	96
12				24	86
13				10	97
14				24	96
15				24	81
16				12	>99
17				24	88
18				24	89

[a] Reaction conditions: aryl halide (0.2 mmol), aryl boronic acid (0.3 mmol), K₂CO₃ (0.3 mmol), solvent (1.5 mL), catalyst (19 ppm Pd). [b] GC yields.

3.3. Recyclability of Pd@CuMoO₄

The recyclability of the Pd@CuMoO₄ catalyst in the Suzuki-Miyaura and Sonogashira-Hagihara reactions under optimal reaction conditions were studied and the progress of the reactions were followed by gas chromatography. After each reaction cycle, the catalyst was removed, washed, dried, and reused for the next cycle (Figure 4). Thus, the catalyst can be recoverable and recyclable for 7 runs with very small decreasing in its efficiency, while in the 8th run the yield decreased to 83-85%.

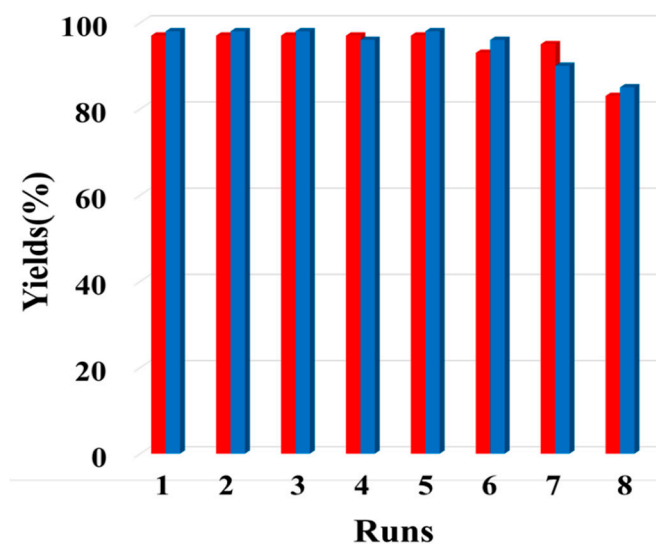


Figure 4. Reusability of the Pd@CuMoO₄ catalyst in the (red) Suzuki-Miyaura coupling reaction of 4-bromobenzaldehyde with phenylboronic acid and (blue) Sonogashira-Hagihara reaction of iodobenzene with phenylacetylene.

In order to find information about stability of the reused catalyst after 8th run in the Suzuki-Miyaura reaction, morphology and physical properties were studied by TEM, SEM, XPS, and EDX-Mapping. In Figure 5, TEM and SEM images shows the presence of tetragonal cubic structures with some elongation in polyoxometalate structures.

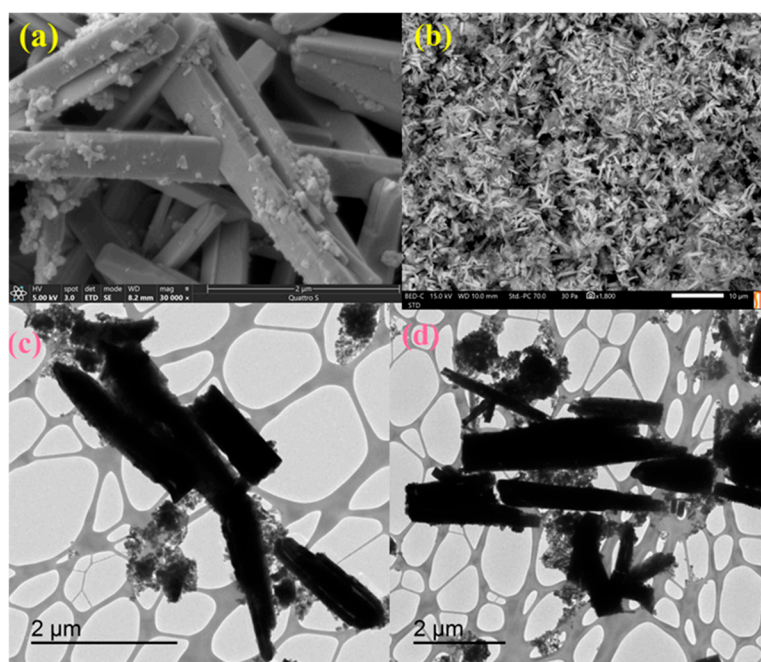


Figure 5. SEM (a, b) and TEM (c, d) images of recycled Pd@CuMoO₄ catalyst.

Also, EDX confirm presence of Pd, Cu and Mo as main elements of the recovered catalyst Pd@CuMoO₄ after 8th runs. Here, these elements are uniformly distributed in the structure (Figure S3 and S4). Finally, XPS of the reused catalyst in the Pd, Cu and Mo regions showed very similar pattern to the pristine catalyst indicating high stability of the Pd@CuMoO₄ during Suzuki-Miyaura coupling reaction (Figure 6).

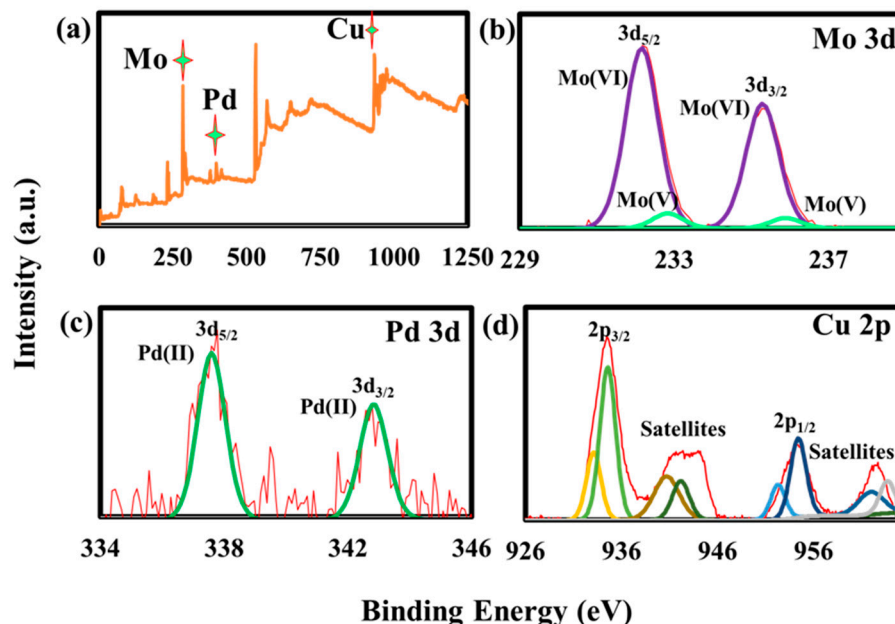


Figure 6. XPS spectrum of recycled Pd@CuMoO₄ catalyst (a) all elements, (b) Mo 3d, (c) Pd 3d, and (d) Cu 2p.

3. Materials and Methods

3.1. Materials

Palladium(II)chloride (PdCl₂), copper(II)nitrate trihydrate Cu(NO₃)₂·3H₂O, sodium molybdate dihydrate (Na₂MoO₄·2H₂O), aryl halides, boronic acids, alkynes and solvents were purchased from Merck, Sigma Aldrich, Across, and TCI companies. The physical morphologies were investigated by a transmission electron microscope (TEM, EOL JEM-2010) and a field emission scanning electron microscope (FE-SEM, JEOL JSM 840). X-ray photoelectron spectroscopy (XPS) measurements were performed in a VGMicrotech Multilab 3000 spectrometer, equipped with an Al anode. The SEM mapping was measured by Hitachi S3000 N. The crystallographic structures of the products were examined by X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 0.154$ Å). ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz, respectively on a Bruker Avance. Reactions were monitored by GC in a Varian CP-3800 apparatus.

3.2. Preparation of Pd@CuMoO₄ Nanostructures

To a 50 mL flask, Cu(NO₃)₂·3H₂O (2.4 mmol, 582 mg), Na₂MoO₄·2H₂O (2.35 mmol, 484 mg), and H₂O (20 mL) were added and the resulting mixture stirred until obtaining a homogeneous solution. In another flask, PdCl₂ (0.08 mmol, 15 mg) was sonicated in H₂O (3 mL) until complete solution and added to the solution containing Cu(NO₃)₂·3H₂O and Na₂MoO₄·2H₂O. The final mixture was stirred for 10 minutes at room temperature. Afterwards, the mixture was transferred to an autoclave reactor and placed at 150 °C for 6 h. Finally, the mixture was subjected to centrifugation, and the resulting solid was washed several times with water and ethanol, and dried in an oven for 24 h, obtaining 385 mg Pd@CuMoO₄.

3.3. General Procedure for the Suzuki-Miyaura Reaction

Aryl halide (0.2 mmol), boronic acids (0.3 mmol), K_2CO_3 (0.3 mmol, 41.4 mg), catalyst (15 mg), H_2O (0.75 mL), and EtOH (0.75 mL) were added to a 5 mL round-bottomed flask and the reaction mixture was stirred at 60 °C for the required reaction time. After completion of the reaction, which was monitored by GC, the organic phase was extracted by ethyl acetate (3×3 mL), and the pure product was obtained by column or plait chromatography using hexane and ethyl acetate as eluents.

3.4. General Procedure for the Sonogashira-Hagihara Reaction

Aryl halide (0.2 mmol), alkyne (0.3 mmol), DABCO (0.3 mmol, 33.6 mg), $Pd@CuMoO_4$ (15 mg) and DMF (1.5 mL) were added to a 5 mL flask and the reaction mixture was stirred at 60 °C for appropriate reaction time. The progress of the reaction was followed by GC. After completing the reaction, the organic phase was extracted by ethyl acetate (3×3 mL), and the pure product was obtained by column or plait chromatography using hexane and ethyl acetate as eluents.

4. Conclusions

In summary, $CuMoO_4$ comprising very low amount of palladium ($Pd@CuMoO_4$) was prepared, characterized and applied as catalyst. $Pd@CuMoO_4$ catalyzed Sonogashira–Hagihara and Suzuki–Miyaura coupling reaction of aryl iodides and bromides at 60–80 °C and very good to excellent yields of desired products were achieved. Contents of Pd in all reactions were in the range of 15–20 ppm. This catalyst was successfully recycled in Suzuki–Miyaura reaction for 7 runs and catalyst preserved its activity.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. **Figure S1.** EDX image of $Pd@CuMoO_4$; **Figure S2.** XRD pattern of $Pd@CuMoO_4$; **Figure S3.** EDX mapping image of recycled $Pd@CuMoO_4$; **Figure S4.** EDX image of recycled $Pd@CuMoO_4$ in the Suzuki–Miyaura reaction of 4-bromobenzaldehyde with phenylboronic acid; Characterization data of Sonogashira–Hagihara and Suzuki–Miyaura coupling reaction's products.

Author Contributions: Conceptualization, M. G.; Methodology, M. G.; validation, H. K. and M. G.; formal analysis, M. G. and J. S.; investigation, H. K.; resources, M. G. and J. S.; data curation, H. K. and M. G.; writing—original draft preparation, M. G.; writing—review and editing, J. S.; visualization, M. G. and J. S.; supervision, M. G.; project administration, M. G.; funding acquisition, M. G. and J. S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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