



Reductive Ullmann-Type Homocoupling of Aryl Halides Catalysed by Mixed Metal Oxide Nanocomposite (Pd/MnFe₂O₄) Under Aqueous Condition

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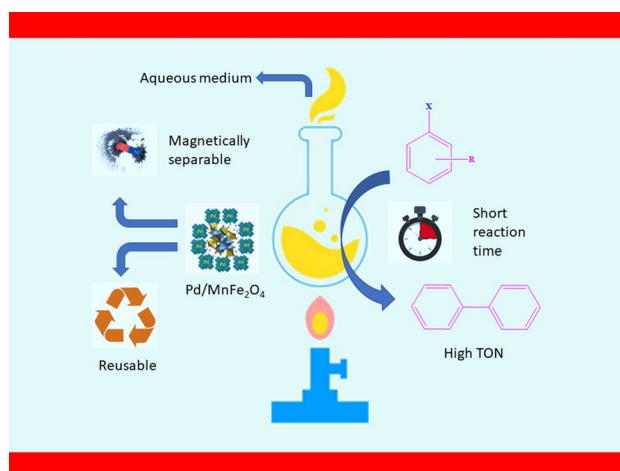
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Abstract

A highly efficient magnetic nanocomposite, Pd/MnFe₂O₄ has been prepared by citrate gel auto combustion and deposition precipitation method for reductive Ullmann homocoupling of aryl halides in an aqueous medium. The physical and chemical properties of the synthesized composite were characterized by XRD, TEM, SEM, EDAX, VSM, and BET analysis. The synthesis of symmetrical biaryls has been achieved at admirable reaction conditions with high yield in a short reaction time. The nanocomposite catalyst could be easily separated by magnetic separation and recycled up to six reaction cycles with appreciable yields of desired products. The synthesized nanocomposite was found to be a best alternative catalyst for carbon–carbon bond formation in Ullmann-type homocoupling.

Graphical abstract



Keywords Aryl halides · Homocoupling · Nanocomposite · Pd/MnFe₂O₄ · Reductive Ullmann

1 Introduction

Supported heterogeneous catalysts have gained much attention in the recent past due to the ease of product separation which enables its recycling, versatility of the supports leading to the adaptability, and variable surface area due to

change in shape and composition thus increasing the overall efficiency to achieve maximum yield [1–3]. The magnetic support has the added advantage of separation of the catalyst by simple mechanical means [4]. Therefore, the recent focus is on the utilization of diverse nanocomposites for improved physical and mechanical properties as well as due to their economic and environmental considerations [5]. Mixed

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metal oxide nanocomposites, especially metal-ferrites, are extensively applied in synthetic organic chemistry due to their high catalytic activity, high surface area and excellent magnetic properties [4, 6, 7].

Palladium is prominently employed in coupling reactions for the formation of C–C, C–N, and C–O types of bonds. The supported palladium catalysts are widely used for the homocoupling of aryl halide for the synthesis of biaryls [8–11]. Aryl-aryl cross or homo-coupling reaction is more convenient and straightforward method for the synthesis of highly functionalized biaryls [12, 13]. The symmetrical biaryl compounds have found wide applications in drug designing, advanced functional materials, agrochemicals, and pharmaceuticals [14, 15]. Over the decades, Ullmann reaction was employed in the direct synthesis of aryl-aryl bonds from aryl halides due to its effectiveness and minimization of undesirable by-products [16, 17]. The synthesis of functionalized biaryls by Ullmann reaction requires relatively harsh reaction conditions [18–25], long reaction time and the presence of an inert atmosphere [19]. In recent past various hybrid materials like hercynite [26], boehmite [27] and CoFe_2O_4 [28] have also been used as catalyst supports to the heterogenization of homogeneous catalysts.

Palladium-catalyzed reductive homocoupling of aromatic halides has been developed as a favourable alternative to the traditional copper-mediated Ullmann reaction [24]. In palladium-catalyzed reductive homocoupling of aryl halides, various reducing agents have been utilized such as a hydrogen donor and/or electron source to regenerate the Pd^0 active species from the Pd^{2+} species to complete the catalytic redox cycle [29, 30]. Hydroquinone [31], alcohols [32], benzoin [33], poly (ethylene glycol) [34], glucose [35], ascorbic acid [36], molecular hydrogen [37], amines [38], formate salt [39, 40], zinc [41], and indium [42] have been used for this purpose. Recently, we have utilized $\text{Pd/MnFe}_2\text{O}_4$ nanocomposite as an efficient catalyst for Suzuki coupling under mild reaction conditions [4] which also can be used effectively for the synthesis of biaryls. Further, the reason for choosing MnFe_2O_4 as catalyst support is because it contains Mn^{2+} and $\text{Fe}_2\text{O}_4^{2-}$ ions which remain inert during the oxidation and reduction steps of the Ullmann coupling. Therefore, in continuation with our recent work on coupling reactions, we extended its application for reductive Ullmann homocoupling of aryl halides in an aqueous medium.

The synthesis of $\text{Pd/MnFe}_2\text{O}_4$ nanocomposite involves the preparation of MnFe_2O_4 by citrate gel auto-combustion method. The Pd-coated MnFe_2O_4 nanocomposite was prepared by deposition precipitation method. Large magnetic anisotropy, high thermal stability, and conspicuous chemical stability provoked us to use MnFe_2O_4 as support [43]. Herein, we demonstrate the catalytic application of a magnetically retrievable $\text{Pd/MnFe}_2\text{O}_4$ nanocomposite for reductive Ullmann homo-coupling reactions of aryl halides for

the construction of biaryl compounds utilizing hydrazine hydrate as an effective reducing agent in aqueous media.

2 Experimental

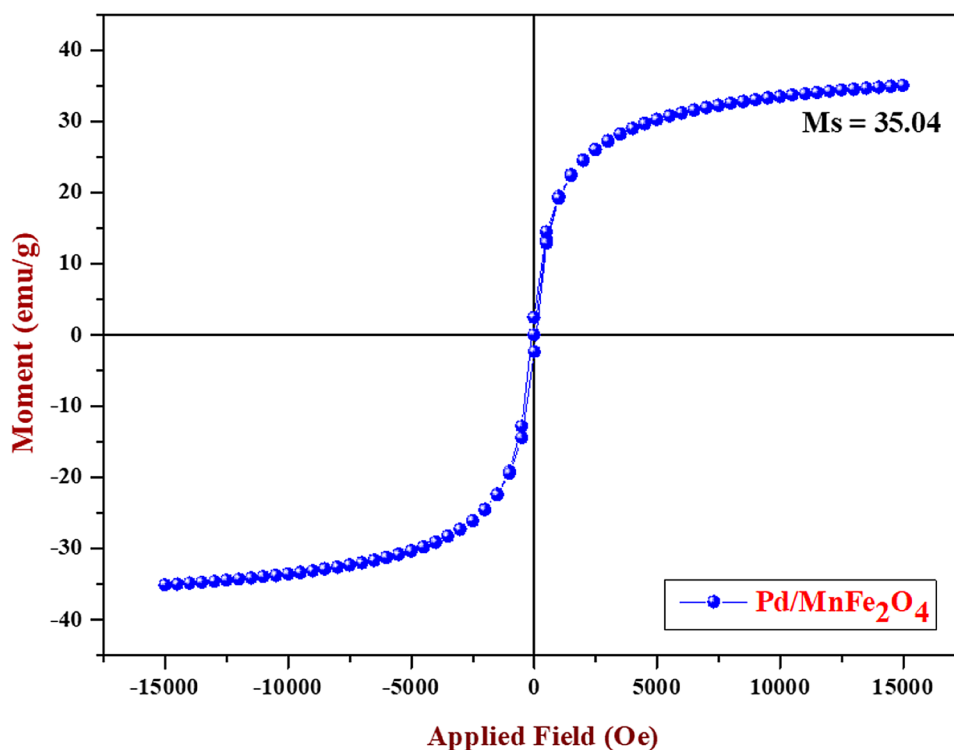
2.1 Materials and Characterization

Aryl halides (Sigma-Aldrich) were utilized as received. Reagent grade iron (III) citrate [$\text{C}_6\text{H}_5\text{FeO}_7$], manganese nitrate [$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], citric acid anhydrous [$\text{C}_6\text{H}_8\text{O}_7$], polyvinyl pyrrolidone (PVP), ammonia (NH_3) and K_2CO_3 were used as received. The melting points of synthesized derivatives were recorded by an open capillary method and are uncorrected. NMR spectra were recorded on Bruker 400 MHz spectrometer (Irradiation frequency: 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) in CDCl_3 using TMS as an internal standard while δ values are expressed in ppm. The crystallographic phase and structural evidence were confirmed by employing an X-ray diffraction technique (D/max-2200 pc, Rigaku, Japan) using $\text{Cu K}\beta$ source of radiation, Hitachi S-4700 SEM instrument was used to investigate the surface morphology of samples. The S-Twin AP Tech., G2mF30, 200 kV Tecnai, USA, was used to perform TEM. The surface area of synthesized nanocomposite was determined by using BET (Quanta chrome NOVA 1000e, USA) and Particle size analyzer and Zeta potential (Malvern-UK, Nano ZS90). VSM analysis was used to study the magnetic feature of as-prepared $\text{Pd/MnFe}_2\text{O}_4$ at room temperature. The $\text{Pd/MnFe}_2\text{O}_4$ displayed a superparamagnetic feature. The saturation magnetization value of pure $\text{Pd/MnFe}_2\text{O}_4$ nanocomposites was to be 35.04 emu/g (Fig. 1). The high saturation magnetization and high magnetic property of $\text{Pd/MnFe}_2\text{O}_4$ nanocomposites are prominent features for magnetic separation and recovery.

2.2 Synthesis and Characterization of Nanocrystalline MnFe_2O_4 and $\text{Pd/MnFe}_2\text{O}_4$ Nanocomposite Catalyst

The crystalline MnFe_2O_4 support has been synthesized by the citrate-gel auto combustion method. The palladium immobilized MnFe_2O_4 nanocomposite was prepared by the deposition-precipitation method [4]. The brief procedure for the synthesis of the catalyst involves mixing stoichiometric quantities of iron citrate and manganese nitrate dissolved in a minimum amount of deionized water followed by the addition of an equimolar amount of citric acid and polyvinyl pyrrolidone (PVP) as a capping agent with constant stirring. The pH of the solution was adjusted to 9–9.5 by dropwise addition of ammonia solution. The resultant sol was heated at 80 °C for 3 h to obtain brown agglomerates of MnFe_2O_4 nanoparticles. The MnFe_2O_4 nanoparticles were crushed and sintered at 300 °C for 2 h. Thus

Fig. 1 Magnetization curve of Pd/MnFe₂O₄ nanocomposite



prepared MnFe₂O₄ (1 g) was dispersed in ethanol (30 mL) for 30 min followed by the addition of 150 mg of PdCl₂ upon continuing sonication for another 30 min. Finally, 3 mL of NH₂NH₂·H₂O was added dropwise to the above mixture followed by sonication for 30 min. The prepared catalyst was simply separated by an external magnet and washed with distilled water and ethanol. The resultant nanocomposite was dried under a vacuum and 50 mg of the catalyst is used for the reductive Ullmann-type homocoupling reaction of aryl halides. The amount of Pd loaded is 0.0247 mmol per 50 mg of MnFe₂O₄. The catalyst MnFe₂O₄ is found to be superparamagnetic as studied by VSM curves (Fig. 1). The catalyst was characterized (Fig. S1–Fig. S5) by XRD, EDS, SEM, TEM and BET analysis [4]. The XRD pattern of the Pd/MnFe₂O₄ indicated cubic spinel structure decorated with face centered cubic Pd nanoparticles. The used catalyst also retained all the XRD patterns showing no change in the structure. The presence of Pd in the used and fresh Pd/MnFe₂O₄ nanocomposite was confirmed through EDS analysis. The spherical shaped Pd nanoparticles were found to be embedded on the 2D nanosheets of MnFe₂O₄ as noticed in SEM and TEM micrographs. A surface area of 44.79 m² g⁻¹ was obtained for Pd/MnFe₂O₄ nanocomposites from BET analysis.

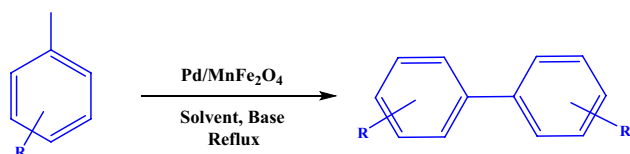
2.3 General Procedure for Reductive Ullmann Homocoupling

A mixture of Pd/MnFe₂O₄ catalyst (50 mg), aryl halide (2 mmol), Hydrazine hydrate (2 mmol), and K₂CO₃

(2 mmol) was added to 25 ml round bottom flask containing 4 ml solvent DMF: Water (1:1). The reaction mixture was then refluxed at the relevant temperature and time. The progress of the reaction was analyzed by TLC (petroleum ether-ethyl acetate 9:1). Upon the completion of the reaction, the mixture was cooled at room temperature. The amount of catalyst used was 50 mg which contains 2.62 mg of Pd corresponding to 0.0247 mmol. Therefore, the Pd catalyst utilized in the present study amounts to 2.47 mol% of the reactants. The catalyst was separated by an external magnet and washed several times with EtOH and water. The reaction mixture was extracted with ethyl acetate (3 × 5 ml) and the combined extract was dried over anhydrous Na₂SO₄. The crude product was obtained after evaporation of the solvent under reduced pressure which was purified by column chromatography (petroleum ether-ethyl acetate, 9:1). The purified product was analyzed by IR and NMR spectroscopy.

3 Results and Discussion

In order to explore the catalytic activity of synthesized Pd/MnFe₂O₄ for reductive Ullmann homocoupling of aryl Iodides and bromides, we initially attempted optimization of reaction conditions (Scheme 1). The model reaction of homocoupling of iodobenzene has been selected for the screening of different reductants solvents, bases as well as reaction temperature.



Scheme 1 Reductive Ullmann-type homocoupling for biaryl synthesis

Table 1 Screening of Reductant for Ullmann-type homocoupling

Sr. no	Reductant	Yield (%) ^a
1	–	No reaction
2	Glucose	70
3	NaBH ₄	54
4	Ascorbic acid	78
5	Hydrazine hydrate	92
6	Glycerol	25
7	Hydroquinone	45

2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄, 2 mmol of a base, 2 mmol reductant and 4 mL solvent

^aIsolated yields

3.1 Effect of Reductant

The reductive Ullmann coupling is influenced by a reducing agent. The role of the reducing agent is to regenerate the active transition metal by reducing its oxidized form during the coupling reaction. Initially, we examined the feasibility of the homo-coupling reaction with several reductants as shown in Table 1. In absence of a reducing agent, the reaction fails to yield the desired product (Table 1, entry 1). Several other reducing agents such as glucose, sodium borohydride, ascorbic acid, hydrazine hydrate, glycerol, and hydroquinone have also been screened (Table 1, entries 2–7). Amongst the above reductants, only water-soluble hydrazine hydrate was capable of providing a good yield of the product only in 1 h. Hydrazine hydrate has a high negative redox potential capable of reducing the high valent metal ions like Pd^{II} and it also acts as a very good ligand [44] thus making the coupling reaction more efficient.

3.2 Effect of Solvent

The effect of solvent for the model reaction of Ullmann homocoupling has been investigated (Table 2). Initially, no significant yields were observed in water, ethanol, acetone, DCM, THF, toluene, and DMSO. A higher yield in DMF (78%) incited to the use of the mixed solvent system (Table 2, entries 8). The mixture of DMF and H₂O (v/v, 1:1)

Table 2 Effect of Solvent for Ullmann-type homocoupling of Iodobenzene

Sr. no	Solvent	Yield (%) ^a
1	H ₂ O	52
2	Ethanol	48
3	Acetone	40
4	DCM	56
5	THF	63
6	Toluene	48
7	DMSO	50
8	DMF	78
9	DMF: H ₂ O (1:1)	94
10	DMF:H ₂ O (8:2)	80

2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄, 2 mmol of a base, 2 mmol reductant, 4 mL solvent

^aIsolated yields

Table 3 Effect of Base on Ullmann-type homocoupling of Iodobenzene

Sr. no	Base	Yield (%) ^a
1	–	37
2	NaOH	60
3	KOH	64
4	Na ₃ PO ₄	60
5	Et ₃ N	54
6	(i-Pr) ₂ NEt	48
7	NaHCO ₃	58
8	K ₂ CO ₃	92
9	CS ₂ CO ₃	80

2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄, 2 mmol of a base, 2 mmol reductant, 4 mL solvent

^aIsolated yields

gave a high yield of the desired product in a short reaction time which was found chosen as the solvent in the present study (Table 2, entry 9).

3.3 Screening of Base

Various organic and inorganic bases were screened to select a suitable one. In absence of a base very low yield of desired product was obtained (Table 3, entry 1). Strong bases such as NaOH and KOH gave moderate yields (Table 3, entries 2–3). Amongst the different bases, K₂CO₃ was found to be an efficient base for the synthesis of the desired product with a high yield (Table 3, entry 8).

3.4 Optimization of Catalyst Amount

For the optimization of amount of catalyst, the reaction was performed using MnFe₂O₄, 20, 30, 40, 50 and 60 mg of Pd/MnFe₂O₄. At optimized conditions Initially we performed the reaction only with MnFe₂O₄. It was found that while use of only MnFe₂O₄ without Pd, product was not formed. As indicated in Table 4, by increasing the quantity of catalyst from 20 to 50 mg the yield was clearly improved along with the Pd mol %. Further increasing the amount of catalyst (60 mg) led to the constant % of yield (Table 4).

3.5 Effect of Temperature

The effect of temperature was also investigated and a suitable temperature range has been elected for homocoupling. The model reaction was performed at a different temperature from 60 to 100 °C and the results are depicted in Fig. 2. The reaction furnished with increased yield as we increase the temperature from 60 to 90 °C. Further, an increase in temperature results in no change in the yield. The study revealed that 90 °C is a remarkable temperature that produced a high yield in a short reaction time.

After optimizing reaction conditions, we explored the scope of the Pd/MnFe₂O₄ nanocomposite catalyst. Various substituted aryl halides (I, Br) have been homocoupled under optimized reaction conditions to result in functional symmetrical biaryls (Scheme 2). The catalyst exhibited remarkable activity for the aromatic halides bearing electron-donating (-Me, -OMe) as well as electron-withdrawing groups (-CHO, -CN, -F) (Table 5, entry 2a–2n). The reaction was smoothly furnished for highly functional aryl halides resulting formation of highly substituted biaryls (Table 5, entry 2o). Alternatively, heterocyclic aryl halides like 2-iodopyridine, 2-bromopyridine, and 5-iodothiophene-2-carbaldehyde provide a good yield of product within 1–1.5 h (Table 5, entry 2p–2r). Aromatic hydrocarbon halides like 1-halo-naphthalenes (I & Br) gave admirable yield (84–88%) in short

Table 4 Optimization of amount of catalyst

Sr. no	Amount of catalyst ^a	Yield ^b (%)
1	50 mg of MnFe ₂ O ₄	No reaction
2	20 mg of Pd/MnFe ₂ O ₄ (Pd 0.98 mol %) ^c	76
3	30 mg of Pd/MnFe ₂ O ₄ (Pd 1.50 mol %) ^c	83
4	40 mg of Pd/MnFe ₂ O ₄ (Pd 1.97 mol %) ^c	87
5	50 mg of Pd/MnFe ₂ O ₄ (Pd 2.47 mol %) ^c	92
6	60 mg of Pd/MnFe ₂ O ₄ (Pd 2.96 mol %) ^c	92

^a2 mmol of Iodobenzene and 2 mmol of a K₂CO₃, 2 mmol hydrazine hydrate, 4 mL 1:1 DMF-H₂O, 90 °C

^bIsolated yields and ^cCalculated from EDAX

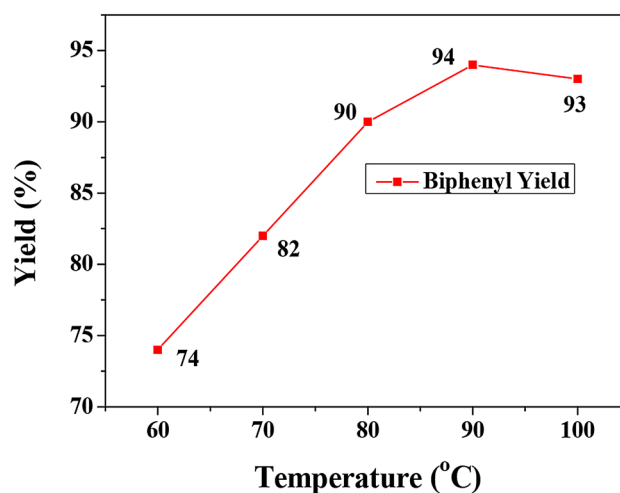
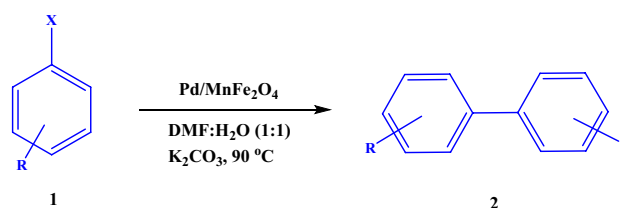


Fig. 2 Effect of Temperature on Ullmann-type homocoupling (2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄, 2 mmol of a base, 2 mmol reductant, 4 mL solvent)

reaction time (Table 5, entry 2s–2t). All the biaryls results with high yield with high TON.

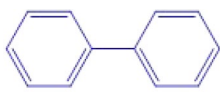
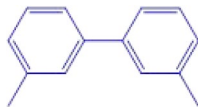
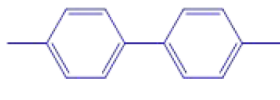
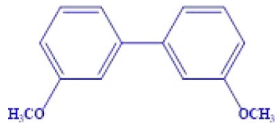
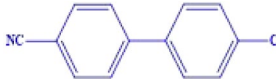

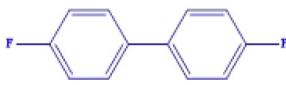
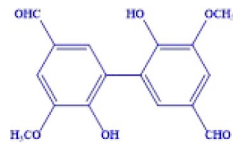
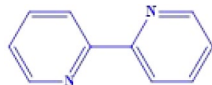
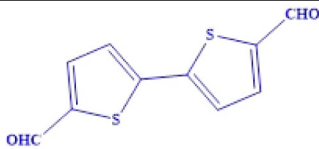
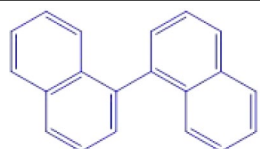
A plausible mechanism for reductive Ullmann homocoupling is depicted in Fig. 3 on basis of previous reports [20]. Initially, oxidative insertion of aryl halide to Pd⁰ of Pd/MnFe₂O₄ nanocomposite catalyst (1), results in the formation of Ar-(Pd^{II})-I (2) species. Nucleophilic substitution of (2) with NH₂NH₂ produces complex (3), oxidative addition of another molecule of aryl halide resulting complex (4) which by reductive elimination generates the desired biaryl product and species (5). Through β-H elimination and reductive elimination, Pd(0) is regenerated from (5) along with the formation of diazene (NH=NH) and HI. Finally, diazene will be removed as nitrogen gas.

A reusability study of synthesized Pd/MnFe₂O₄ nanocomposite has also been performed. The Pd/MnFe₂O₄ nanocomposite was separated from the reaction mixture by an external magnet after completion of the reaction and washed with water, ethanol, and ethyl acetate. The obtained catalyst was then employed for the next reaction cycles. Interestingly, the recovered Pd/MnFe₂O₄ catalyst could preserve the catalytic activity without much degradation in six successive reaction runs as shown in Table 6. The efficacy of reusability



Scheme 2 Ullmann-type reductive homocoupling of aryl halides

Table 5 Pd/MnFe₂O₄ Catalyzed Ullmann homocoupling of aryl halides^a

		
2a , X = I, 94%, 1 h, 3805	2c , X = I, 79%, 2.5 h, 3198	2e , X = I, 93%, 1.5 h, 3765
2b , X = Br, 92%, 1 h, 3724	2d , X = Br, 78%, 3 h, 3157	2f , X = Br, 90%, 2 h, 3643
		
2g , X = I, 90%, 1 h, 3643	2i , X = I, 96%, 1 h, 3886	2k , X = I, 90%, 1.5 h, 3643
2h , X = Br, 89%, 1h, 3603	2j , X = Br, 96%, 1 h, 3886	2l , X = Br, 86%, 2 h, 3481
		
2m , X = I, 92%, 1.5 h, 3724	2o , X = I, 86%, 1 h, 3481	2p , X = I, 84%, 1 h, 3400
2n , X = Br, 92%, 1.5 h, 3724		2q , X = Br, 84 %, 1.5 h, 3400
		
2r , X = I, 91%, 1 h, 3684	2s , X = I, 80%, 1 h, 3238	
	2t , X = Br, 80%, 1 h, 3238	

^a2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄ (Pd loading was calculated to be 2.47 mol.% based on EDX analysis), and 2 mmol of a base, 2 mmol hydrazine hydrate, 4 mL solvent.
^bIsolated yields, last number indicates TON.

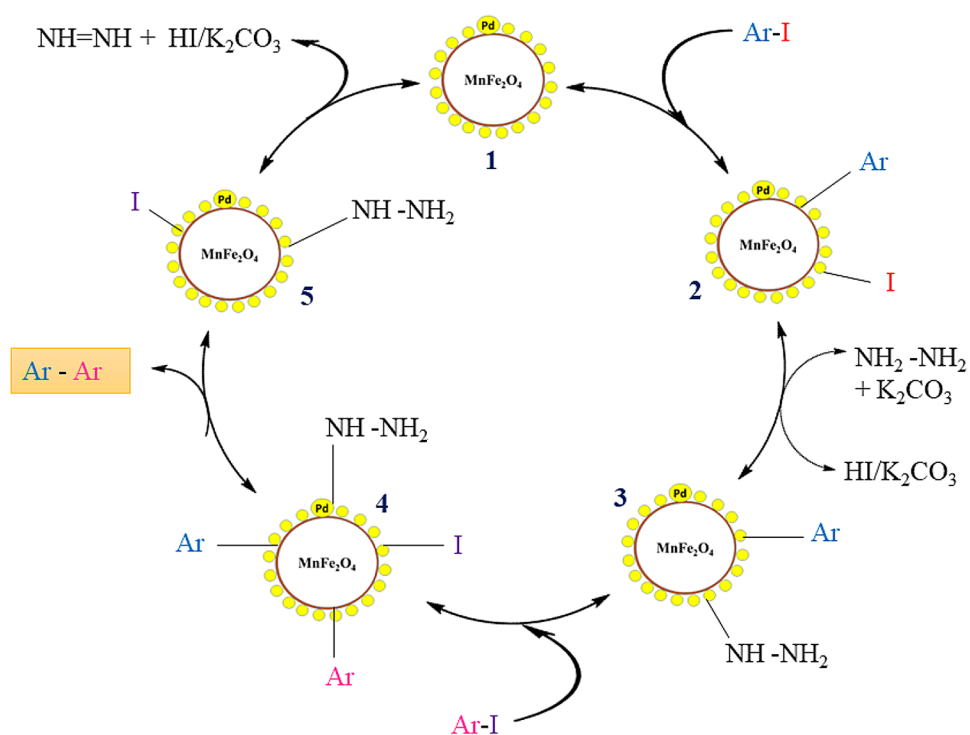
of Pd/MnFe₂O₄ nanocomposite was further confirmed by XRD and EDX analysis of reused catalysts. XRD pattern of the reused catalyst indicates that the morphology and peak position were found very similar to that of the fresh catalyst (Fig. 4). The palladium content of reused catalyst after six runs was determined by EDX analysis which indicates there is not much leaching of Pd (Fig. 4). The study revealed the high stability and reusability of the Pd/MnFe₂O₄ nanocomposite.

The catalytic efficiency of synthesized Pd/MnFe₂O₄ nanocomposite catalyst has been examined by comparing it with other reported catalysts [20, 31, 33, 41–45] for reductive Ullmann homocoupling (Table 7). From the result obtained by comparison study, it is revealed that the Pd/MnFe₂O₄ catalyst using NH₂NH₂ as reductant was found to be highly

efficient with respect to reaction conditions, the yield of the product, and time for the reaction.

4 Conclusion

Pd/MnFe₂O₄ nanocomposite has been successfully prepared by citrate gel auto combustion and deposition–precipitation method. The Physicochemical study of the synthesized nanocomposite was characterized by XRD, SEM, TEM, EDX, and BET. The magnetically separable and reusable Pd/MnFe₂O₄ nanocomposite is utilized as a

Fig. 3 Plausible mechanism for reductive Ullmann Homocoupling**Table 6** Reusability of Pd/MnFe₂O₄ nanocomposite for reductive Ullmann Homocoupling

Reaction cycle	1	2	3	4	5	6
Yield (%) ^a	94	93	92	90	88	84

2 mmol of aryl halide, 50 mg of Pd/MnFe₂O₄, 2 mmol of a base, 2 mmol reductant and 4 mL solvent

^aIsolated yields

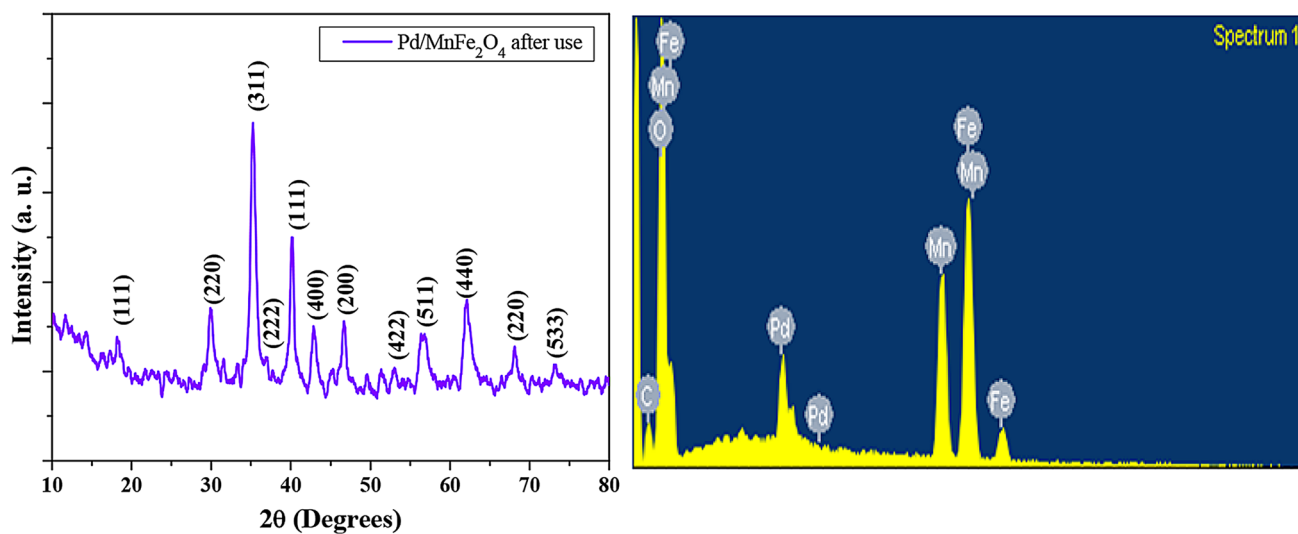
**Fig. 4** X-ray diffraction patterns and EDX spectrum of reused Pd/MnFe₂O₄ nanocomposite

Table 7 Comparative study of Pd/MnFe₂O₄ nanocomposite with reported catalysts

Sr. No	Catalyst	Reducing agent	Conditions	Time (h)	Yield (%)	Refs.
1	Pd(OAc) ₂	Hydroquinone	Cs ₂ CO ₃ , 100 °C, N,N-dimethylacetamide(DMA)	16	90	[31]
2	Pd(OAc) ₂	N ₂ H ₄ ·H ₂ O	K ₃ PO ₄ , RT, DMF:DMSO	8	85	[44]
3	Pd/PCMS	Glycol	CH ₃ CO ₂ K, 110 °C, DMSO	10	90	[45]
4	Pd@PANIs	N ₂ H ₄ ·H ₂ O	(i-Pr) ₂ Net, 140 °C, N-methyl pyrrolidone	24	74	[20]
5	Ni(cod) ₂	N ₂ H ₄ ·H ₂ O	K ₃ PO ₄ , 1,4-dioxane, 110 °C	12	81	[46]
6	Pd@poly-CN-PF ₆	Ascorbic acid	NaOH, Water, 100 oC	9	93	[30]
7	Pd/MnFe ₂ O ₄	N ₂ H ₄ ·H ₂ O	K ₂ CO ₃ , 90 °C, DMF:H ₂ O (1:1)	1	94	This work

heterogeneous catalyst in aqueous solutions. The developed nanocomposite exhibited excellent catalytic activity for the synthesis of symmetric biaryls via the Ullmann homocoupling using hydrazine hydrate as the reducing reagent. Additionally, the catalyst was chemically stable and could be recycled six times without significant loss in its activity.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10562-023-04378-z>.

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Author contributions DJS: methodology, data curation, investigation, writing original draft. SNZ: supervision, data curation, investigation. PMM: methodology, data curation, investigation. DMP: supervision, data curation, investigation. AST: data curation, formal analysis. GSG: supervision, methodology, visualization, investigation, writing – review & editing.

Declarations

Conflict of interest The authors declare that there is no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Sharma N, Ojha H, Bharadwaj A, Pathak DP, Sharma RK (2015) Preparation and catalytic applications of nanomaterials: a review. *RSC Adv* 5:53381–53403
- Shojaei AF, Tabatabaeian K, Zanjanchi MA, Moafi HF, Modirpanah N (2015) Synthesis, characterization and study of catalytic activity of Silver doped ZnO nanocomposite as an efficient catalyst for selective oxidation of benzyl alcohol. *J Chem Sci* 127:481–491
- Raji V, Chakraborty M, Parikh PA (2012) Catalytic performance of silica-supported silver nanoparticles for liquid-phase oxidation of ethylbenzene. *Ind Eng Chem Res* 51:5691–5698
- Sutar DJ, Zende SN, Kadam AN, Mali MG, Mhaldar PM, Tapase AS, Bathula C, Lee S, Gokavi GS (2023) *J Organomet Chem* 983:122541
- Chng LL, Erathodiyil N, Ying JY (2013) Nanostructured catalysts for organic transformations. *Acc Chem Res* 46:1825–1837
- Samantaray S, Pradhan DK, Hota G, Mishra BG (2012) Catalytic application of CeO₂-CaO nanocomposite oxide synthesized using amorphous citrate process toward the aqueous phase one pot synthesis of 2-amino-2-chronenes. *Chem Eng J* 193–194:1–9
- Li S, Zhang W, So MH, Che CM, Wang R, Chen R (2012) One-pot solvothermal synthesis of Pd/Fe₃O₄ nanocomposite and its magnetically recyclable and efficient catalysis for Suzuki reactions. *J Mol Catal A-Chem* 359:81–87
- Biswas S, Pal A, Pal T (2020) Supported metal and metal oxide particles with proximity effect for catalysis. *RSC Adv* 10:35449–35472
- Yeo KM, Lee SI, Lee YT, Chung YK, Lee IS (2008) Core-satellite heterostructure of Fe₃O₄-Pd nanocomposite: Selective and magnetically recyclable catalyst for decarboxylative coupling reaction in aqueous media. *Chem Lett* 37:116–117
- Trzeciak AM, Ziolkowski JJ (2005) Structural and mechanistic studies of Pd-catalyzed C–C bond formation: the case of carbon-ylation and Heck reaction. *Coord Chem Rev* 249:2308–2322
- Yin L, Liebscher J (2007) Carbon–carbon coupling reactions catalyzed by heterogeneous palladium catalysts. *Chem Rev* 107:133–173
- Dubey AV, Kumar AV (2020) A bio-inspired magnetically recoverable palladium nanocatalyst for the ullmann coupling reaction of aryl halides and aryl boronic acids in aqueous media. *Appl Organomet Chem* 34:1–10
- Vasconcelos SNS, Reis JS, de Oliveira IM, Balfour MN, Stefani HA (2019) Synthesis of symmetrical biaryl compounds by homocoupling reaction. *Tetrahedron* 75(2019):1865–1959
- Hegde RV, Ghosh A, Patil SA, Dateer RB (2019) Pd-nanoparticles catalyzed denitrogenative coupling of aryl halides with arylhydrazines: Greener approach for biaryls synthesis under ligand-free condition. *Tetrahedron* 75:130777
- Nagaraju K, Ma D (2018) Oxidative coupling strategies for the synthesis of indole alkaloids. *Chem Soc Rev* 47:8018–8029
- Crabbe BW, Kuehm OP, Bennett JC, Hallett-Tapley GL (2018) Light-activated Ullmann homocoupling of aryl halides catalyzed using gold nanoparticle-functionalized potassium niobium oxides. *Catal Sci Technol* 8:4907–4915
- Layek K, Maheswaran H, Kantam ML (2013) Ullmann coupling of aryl iodides catalyzed by gold nanoparticles stabilized on nanocrystalline magnesium oxide. *Catal Sci Technol* 3:1147–1150

18. Mosaddegh N, Yavari I (2018) Pd-poly(N-vinyl-2-pyrrolidone)/MCM-48 nanocomposite: a novel catalyst for the Ullmann reaction. *Chem Zvesti* 72:2013–2021
19. Wang W, Chen S, Cal EG, Moro MM, Moya S, Coy E, Wang C, Hamon JR, Astruc D (2020) ZIF-8-based vs. ZIF-8-derived Au and Pd nanoparticles as efficient catalysts for the Ullmann homocoupling reaction. *Inorg Chem Front* 7:3945–3952
20. Liu Y, Tang D, Cao K, Yu L, Han J, Xu Q (2018) Probing the support effect at the molecular level in the polyaniline-supported palladium nanoparticle-catalyzed Ullmann reaction of aryl iodides. *J Catal* 360:250–260
21. Mullick K, Biswas S, Kim C, Ramprasad R, Angeles-Boza AM, Suib SL (2017) Ullmann reaction catalyzed by heterogeneous mesoporous copper/manganese oxide: a kinetic and mechanistic analysis. *Inorg Chem* 56:10290–10297
22. Rovira M, Jašíková L, Andris E, Acuña-Parés F, Soler M, Güell I, Wang MZ, Gómez L, Luis JM, Roithová J, Ribas X (2017) A Cu^I/Cu^{III} prototypical organometallic mechanism for the deactivation of an active pincer-like CuI catalyst in Ullmann-type couplings. *Chem Commun* 53:8786–8789
23. Chen T, Chen BT, Bukhryakov KV, Rodionov VO (2017) Thiols make for better catalysts: Au nanoparticles supported on functional SBA-15 for catalysis of Ullmann-type homocouplings. *Chem Commun* 53:11638–11641
24. Li M, Xing X, Ma Z, Lv J, Fu P, Li Z (2018) Synthesis of composition tunable and (111)-faceted Cu/Cu₂O nanoparticles toward photocatalytic, ligand-free, and solvent-free C–N ullmann coupling reactions. *ACS Sustain Chem Eng* 6:5495–5503
25. Hajipour AR, Rezaei F, Khorsandi Z (2017) Pd/Cu-free Heck and Sonogashira cross-coupling reaction by Co nanoparticles immobilized on magnetic chitosan as reusable catalyst. *Green Chem* 19:1353–1361
26. Mohamadi M, Ghorbani-Choghamarani A (2020) L-Methionine-Pd complex on mercynite as a highly efficient and reusable nanocatalyst for C–C cross-coupling reactions. *New J Chem* 44:2919–2929
27. Ghorbani-Choghamarani A, Mohamadi M, Hudson RHE, Tamoradi T (2019) Boehmite@tryptophan-Pd nanoparticles: a new catalyst for C–C bond formation. *Appl Organometal Chem* 44:e4977
28. Tamoradi T, Mousavi SM, Mohamadi M (2020) C–C and C–S coupling catalyzed by supported Cu(II) on nano CoFe₂O₄. *Chemistry Select* 5:5077–5081
29. Iranpoor N, Firouzabadi H, Ahmadi Y (2012) Carboxylate-based, room-temperature ionic liquids as efficient media for palladium-catalyzed homocoupling and sonogashira–Hagihara reactions of aryl halides. *Eur J Org Chem* 2:305–311
30. Wang J, Li Y, Li P, Song G (2013) Polymerized functional ionic liquid supported Pd nanoparticle catalyst for reductive homocoupling of aryl halides. *Monatsh Chem* 144:1159–1163
31. He HS, Zhang C, Ng CKW, Toy PH (2005) Polystyrene-supported triphenylarsines: useful ligands in palladium-catalyzed aryl halide homocoupling reactions and a catalyst for alkene epoxidation using hydrogen peroxide. *Tetrahedron* 61:12053–12057
32. Shao L, Du Y, Zeng M, Li X, Shen W, Zuo S, Lu Y, Zhang XM, Qi C (2010) Ethanol-promoted reductive homocoupling reactions of aryl halides catalyzed by palladium on carbon (Pd/C). *Appl Organomet Chem* 24:421–425
33. Park BR, Kim KH, Kim TH, Kim JN (2011) Palladium-catalyzed benzoin-mediated redox process leading to biaryls from aryl halides. *Tetrahedron Lett* 52:4405–4407
34. Wang L, Zhang Y, Liu L, Wang Y (2006) Palladium-catalyzed homocoupling and cross-coupling reactions of aryl halides in poly(ethylene glycol). *J Org Chem* 71:1284–1287
35. Monopoli A, Calò V, Ciminale F, Cotugno P, Angelici C, Cioffi N, Nacci A (2010) Glucose as a clean and renewable reductant in the pd-nanoparticle-catalyzed reductive homocoupling of bromo- and chloroarenes in water. *J Org Chem* 75:3908–3911
36. Ram RN, Singh V (2006) Palladium (II) chloride/EDTA-catalyzed biaryl homo-coupling of aryl halides in aqueous medium in the presence of ascorbic acid. *Tetrahedron Lett* 47:7625–7628
37. Mukhopadhyay S, Rothenberg R, Wiener H, Sasson Y (1999) Palladium-catalyzed aryl-aryl coupling in water using molecular hydrogen: Kinetics and process optimization of a solid-liquid-gas system. *Tetrahedron* 55:14763–14768
38. Kuroboshi M, Waki Y, Tanaka H (2003) Palladium-catalyzed tetrakis(dimethylamino)ethylene-promoted reductive coupling of aryl halides. *J Org Chem* 68:3938–3942
39. Mukhopadhyay S, Rothenberg G, Qafisheh N, Sasson Y (2001) Supported phase-transfer catalysts as selective agents in biphenyl synthesis from haloaryls. *Tetrahedron Lett* 42:6117–6119
40. Wan Y, Chen J, Zhang D, Li H (2006) Ullmann coupling reaction in aqueous conditions over the Ph-MCM-41 supported Pd catalyst. *J Mol Catal A-Chem* 258:89–94
41. Li J, Xie Y, Yin D (2003) New role of CO₂ as a selective agent in palladium-catalyzed reductive ullmann coupling with zinc in water. *J Org Chem* 68:9867–9869
42. Phil HL, Seomoon D, Lee K (2005) Palladium-catalyzed inter- and intramolecular coupling reactions of aryl and vinyl halides mediated by indium. *Org Lett* 7:343–345
43. Jadhav VG, Sarode SA, Nagarkar JM (2015) Palladium on manganese ferrite: An efficient catalyst for ligand free decarboxylative Sonogashira reaction with arene diazonium tetrafluoroborate. *Tetrahedron Lett* 56:1771–1774
44. Gong X, Wu J, Meng Y, Zhang Y, Ye LW, Zhu C (2019) Ligand-free palladium catalyzed Ullmann biaryl synthesis: “Household” reagents and mild reaction conditions. *Green Chem* 21:995–999
45. Zeng M, Zhang X, Shao L, Qi C, Zhang XM (2012) Highly porous chitosan microspheres supported palladium catalyst for coupling reactions in organic and aqueous solutions. *J Organomet Chem* 704:29–37
46. Lv L, Qiu Z, Li J, Liu M, Li CJ (2018) N₂H₄ as traceless mediator for homo- and cross- aryl coupling. *Nat Commun* 9:1–11

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