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The first report of hercynite as a solid support, L-methionine-Pd complex supported on hercynite as highly efficient reusable nanocatalyst for C-C cross coupling reactions

Masoud Mohammadi, Arash Ghorbani-Choghamarani*

In this work, a green method was suggested for the synthesis of hercynite magnetic nanoparticles (MNPs) as a novel heterogeneous catalytic support in order to immobilize the homogeneous complexes. In this sense, the study aims at immobilizing L-Methionine-Pd complex on the surface of hercynite MNPs. L-Methionine-Pd which was immobilized on hercynite MNPs surface by a simple, fast, and convenient route. The structure and composition of the prepared Hercynite@L-Methionine-Pd MNPs were completely characterized by XRD, EDX, ICP, SEM, X-ray mapping and TGA and VSM techniques. Besides, it was applied as a green nanocatalyst for Suzuki and Heck cross coupling reactions under green conditions. The Hercynite@L-Methionine-Pd MNPs offer several advantages i.e. simple synthesis method under green conditions, thermal and chemical stability during organic reactions, short reaction times, high yields of the products, excellent selectivity and easy work-up procedure. Moreover, the recycled nanocatalyst was reused for at least five cycles with no significant loss of its activity. Hot filtration test indicated heterogeneous catalysis for both of the mentioned reactions. This work is useful for the development and application of the magnetically recoverable Pd nanocatalyst on the chemistry basis of green principles.

Introduction

Belonging to the most important methodologies of the modern catalytic organic synthesis, the C-C cross coupling reactions between different aryl halide derivatives with aryl boronic acids (Suzuki reaction) or olefins (Heck reaction), catalyzed by a transition-metal catalyst (specially Palladium) under mild reaction conditions, have received profound attention due to their one-step procedure¹, no need to isolate the intermediate ², high yields of the products ^{2,3}, good reactivity of a less reactive aryl halide ², good selectivity ⁴ and broad range of functional groups⁵.

These synthetic techniques have been widely used in industrial and laboratorial scale for the synthesis of important natural products for example, in medicinal chemistry ^{3,6}. In this sense, C-C coupling reactions have been frequently used in the synthesis of important bioactive compounds and drugs⁷. It is worth mentioning that the Nobel Prize in chemistry 2010 was awarded jointly to Akira Suzuki, Richard f. Heck, and Ei-ichi Negishi for palladium-catalyzed C-C cross couplings in organic synthesis^{8,9}. This significant success fully demonstrates the importance of developing C-C cross coupling reactions in the current modern organic chemistry.

The use of nanotechnology and benign and clean synthetic procedures is one of the most important ways to reduce environmental concerns. The development of appropriate and efficient methods for the synthesis of nanometer-sized materials has a special place in the scientific community ¹⁰. During recent years, heterogeneous nanomaterials have been successfully applied as support for the heterogenization of homogeneous catalysts by the immobilization of homogeneous organometallic complexes, acid and base on the heterogeneous nanomaterials such as (heteropoly acids¹¹, silica nanoparticles¹², SBA-15 ¹³, SBA-16 ¹⁴⁻¹⁶, MCM-41 ¹⁷⁻¹⁹, MCM-48 ¹⁶, FSM-16 ^{20–22}, ZIF-8 ^{23–25}, alumina ^{26–28}, Boehmite ^{2,29}, graphene oxide ^{30,31}, polymers ³², Biochar ^{33–37} peptide nanofibers ³⁸, Fe₃O₄ ³⁹⁻⁴⁵, Fe₃O₄@SBA-15 ⁴⁶⁻⁴⁸, Fe₃O_{4@}MCM-41⁴⁹, Fe₃O₄@FSM-16 50 , Fe₃O₄@Boehmite 51 , Fe₃O₄@ZIF-8 52 and spinel ferrites MNPs ^{53,54}. Introducing the novel and stable heterogeneous catalytic supports is a hot research topic in industrial and catalysis science. The Spinel ferrites, (AB2O4, which represents one or more bivalent transition metals such as , Al ⁵⁴, Ni ⁵⁵, Co ⁵⁶, Cu ⁵⁷, Zr ⁵³, Zn ⁵⁸, Fe⁴⁴, Mn ⁵⁹, Bi ⁶⁰ etc.), due to their magnetic properties and thermal and chemical stability, have become significant and efficient tools in modern catalytic organic synthesis^{53,54}. In this category, Hercynite (FeAl₂O₄) is a normal spinel ferrite with all or most of the aluminium ions (Al⁺³) ions on both octahedral (B sites) and the ferrous (Fe⁺²) ions occupying tetrahedral sites (A sites), while oxygen occupies FCC sites 54,61. However, some ferric ions

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(Fe³⁺) may be located in its structure ⁶¹, and in order to

overcome this drawback, the synthesis of hercynite MNPs

requires oxygen-free conditions to prevent oxidation of Fe⁺²

ions to ions Fe^{3+ 62}. Hercynite nanoparticles have received

profound attention due to their moderate saturation

magnetization (because of the presence of iron oxide) ⁶³, high

concentration of surface OH groups⁵⁴, high specific surface

area 54, high ductility (fracture-mechanical strength) and

flexibility against spalling and cracking ⁶¹ and excellent

chemically, mechanically and thermally stabilities (compared

to Fe₃O₄) ⁵⁴. Given the mentioned features, the use of

hercynite MNPs as a novel heterogeneous support for the

immobilization of homogeneous catalysts seems attractive.

According to the best of our knowledge, this is the first report

on the immobilization of homogeneous complex on the

In the development of green chemistry principles; herein,

hercynite MNPs were introduced as a novel heterogeneous

catalytic support for the immobilization of L-Methionine-Pd

complex. Hercynite@L-Methionine-Pd nanoparticles were

efficiently applied as a reusable catalyst for the Suzuki and Heck C-C cross coupling reactions under green conditions.

Preparation of L-Methionine-Pd heterogenized complex supported

on the surface of hercynite magnetic nanoparticles (Hercynite@L-

The hercynite magnetic nanoparticles were prepared by the

coprecipitation technique as it was previously reported ⁵⁴. A

mixture of Al(NO₃)₃·9H₂O (2 mmol) and FeCl₂·4H₂O (4 mmol)

was dissolved in 100 mL of water and stirred at 80 °C under N₂

protection. In the next step, 10 mL of aqueous NaOH solution

(0.2 M) was added to the reaction mixture (the pH of solution

was found to be 12). After 30 min of stirring the mixture, an

external magnet collected the prepared hercynite MNPs which

were washed with deionized water and ethanol few times and,

then, dried at 75 °C in an oven for 4 h. In order to immobilize the L-Methionine amino acid on the surface of hercynite

heterogeneous support, 1 g of the prepared hercynite

nanoparticles was dispersed in 50 mL water by sonication for

30 min. and, then, L-Methionine (2.5 mmol) was added to the

reaction mixture which was stirred under the N₂ atmosphere

at reflux conditions for 24 h. Afterwards, the obtained

Hercynite@L-Methionine MNPs were washed with hot

deionized water and hot ethanol few times and, then, dried at

75 °C in an oven for 4 h. Finally, in order to synthesize the

target Hercynite@L-Methionine-Pd heterogenized complex,

0.5 g of Hercynite@L-Methionine MNPs was dispersed in 30

mL ethanol by sonication for 30 min and, then, Pd(OAc)₂ (0.25

g) was added to the reaction mixture. Subsequently, it was

stirred under the N₂ atmosphere at 80 °C for 24 h. In the next

step, 3 mmol of NaBH₄ was added to the reaction and stirred

for 2 more hours. Then, the obtained Hercynite@L-

Methionine-Pd MNPs were separated using an external

surface of hercynite as support.

Experimental

Methionine-Pd)

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magnet, washed with water and ethanol and dried at 80 °C in DOI: 10.1039/C9NJ05325E an oven for 12h.

2.2 | General procedure for the Suzuki reaction

A mixture of Phenylboronic acid (1 mmol), aryl halide (1 mmol), K₂CO₃ (3 mmol) and Hercynite@L-Methionine-Pd (0.1 mol %) was dissolved in 3 mL ethanol and stirred at 80 °C under reflux conditions. The progress of the reaction was monitored by TLC. Upon the completion of the reaction, the mixture was cooled down to room temperature and the catalyst was separated by magnetic separation technique, and washed with EtOAc. Finally, the reaction mixture was extracted with H₂O and EtOAc. The organic layer was dried over Na₂SO₄. Finally, the solvent was evaporated, and the corresponding pure products were obtained in excellent yields.

General procedure for the Heck reaction

A mixture of buthyl acrylate (1.2 mmol), aryl halide (1 mmol) and K₂CO₃ (3 mmol) was dissolved in 2 mL PEG-400 and ,then, Hercynite@L-Methionine-Pd (0.125 mol %) was added to the flask and, finally, the mixture was stirred at 80 °C under reflux conditions. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated from the reaction mixtire via magnetic separation technique; the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over Na₂SO₄. Finally, the solvent was evaporated and the corresponding pure products were consequently obtained.

Selected spectral data

4-methylbiphenyl: ¹H NMR (300 MHz, CDCl₃) δ (ppm) = 7.66-7.61 (m,2H), 7.55-7.52 (m, 2H), 7.49-7.44 (m, 2H), 7.38-7.333 (m,1H), 7.30- 7.227 (m,2H), 2.43(s, 3H, Me).

3-methoxybiphenyl: ¹H NMR (300 MHz, CDCl₃) δ (ppm) = 7.63-7.55(m, 2H), 7.48-7.34(m, 2H), 7.21-7.18(m, 2H),7.22-7.14(t, J=2, 1H), 6.94-6.90(m, 1H), 3.01(s,1H)

4-methoxybiphenyl: ¹H NMR (300 MHz, CDCl₃) δ (ppm) = 7.60-7.53(m, 4H), 7.45(t, J=7.5, 2H), 7.35(t, J=7.2, 1H), 7.03-6.98(m, 2H), 3.88(s, 3H)

4-Nitro-1,1'-biphenyl: ¹H NMR (300 MHz, CDCl₃) δ (ppm) = 8.34-8.31 (d, J = 8 Hz, 2H), 7.78-7.75 (d, J = 12 Hz, 2H), 7.67-7.65 (d, J = 12Hz, 2H), 7.55-7.51 (m, 2H) 7.50-7.45 (m, 1H).

Results and discussion

Catalyst preparation

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In this research project, L-Methionine-Pd complex, which was immobilized on the surface of hercynite magnetic nanoparticles (Hercynite@L-Methionine-Pd) has been introduced as a reusable magnetic nanocatalyst. Initially, the hercynite MNPs have been easily prepared in water by coprecipitation technique. It is worth to mention that in the synthesis of spinel ferrite materials some ferric ions (Fe³⁺) may be located in their structure, and, in order to overcome this drawback, hercynite nanoparticles were appended under N₂ atmosphere (oxygen-free conditions) to prevent oxidation of Fe⁺² to Fe³⁺ ions. Then, L-Methionine ligand has been grafted on the surface of hercynite MNPs in green conditions. Finally, the L-Methionine-Pd complex was synthesized by the reaction of Hercynite@L-Methionine-Pd with Palladium (II) acetate (Scheme 1).



Scheme 1 The synthesis of Hercynite@L-Methionine-Pd nanoparticles.

Catalyst characterizations

The as-prepared Hercynite@L-Methionine-Pd catalyst was characterized by XRD, EDS, ICP, SEM, X-ray mapping, TGA, and VSM techniques.

The X-ray diffraction analysis (XRD) patterns of hercynite and Hercynite@L-Methionine-Pd are shown in Figure 1. As it can be seen from Figure 1 (red pattern), the successful synthesis of hercynite MNPs was justified by the XRD peak positions at 2θ = 30.59, 32.15, 35.99, 43.65, 45.87, 54.11, 57.61, 63.27, 71.81, 74.65 and 75.70, which are related to (2 0 0), (0 3 1), (3 1 1), (4 0 0), (1 1 0), (4 2 2), (1 1 1), (4 4 0), (6 2 0), (5 3 3) and (1 1 1) reflections, respectively. 54 Moreover, Hercynite@L-Methionine-Pd (Figure 1 green pattern) displays 11 characteristic peaks at 2θ = 30.38, 31.43, 35.73, 39.68, 43.33, 45.65, 53.83, 57.33, 62.93, 71.04, and 74.39, which were in agreement with the prepared hercynite XRD standard data. On the other hand, it can be found that the surface modification of the hercynite nanoparticles does not lead to change its crystalline phase. Other peaks at 20 values of 39.68°, 45.65° and 65.93° confirmed the presence of Pd(0) in Hercynite@L-Methionine-Pd complex ^{2,64}.



Fig. 1 The XRD patterns of hercynite and Hercynite@L-Methionine-Pd nanocatalyst.

Fig. 2 exhibits the TGA diagram of Hercynite@L-Methionine-Pd. The main weight loss, which was observed between 200 and 550 °C is about 26.61 % and is related to the decomposition of organic moieties on the surface of the hercynite MNPs. The obtained results from TGA analysis confirmed the successful supporting of L-Methionine-Pd on the surface of hercynite.



Fig. 2 TGA curve of Hercynite@L-Methionine-Pd nanocatalyst.

The energy dispersive X-ray spectroscopy (EDS) analysis of Hercynite@L-Methionine-Pd nano catalyst are shown in Fig 3. The presence of Fe, Al, O, C, N, S and Pd in EDX pattern provides evidences confirming the successful synthesis of Hercynite@L-Methionine-Pd. In addition, the exact amount of Pd, which was

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immobilized on Hercynite@L-Methionine, was obtained by ICP-OSE: 1.21 × 10-3 mol g-1.

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Fig. 3 The EDX image of Hercynite@L-Methionine-Pd nanocatalyst

DOI: 10.1039/C9NJ05325E The morphology of the hercynite MNPs (a) and Hercynite@L-Methionine-Pd (b) as probed by the scanning electron microscopy (SEM) technique is shown in Fig 4. SEM images show that most of the prepared nanoparticles were formed in approximately spherical shape and uniform nanometer size for most particles.



Fig. 3 SEM images of hercynite and Hercynite@L-Methionine-Pd nanocatalyst at different magnifications.

The X-ray mapping of Hercynite@L-Methionine-Pd magnetic nanocatalyst is shown in Fig 5. The elemental map images show the good dispersion of Fe, Al, C, N, S and Pd on the surface of the

catalyst, confirming the formation of the heterogeneous L-Methionine-Pd catalyst on the surface of hercynite.

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Fig. 5 EDX-mapping analysis of Hercynite@L-Methionine-Pd nanocatalyst.

Fig 6 exhibits the magnetization curves of hercynite MNPs (a), Hercynite@L-Methionine-Pd complex (b) and the recovered Hercynite@L-Methionine-Pd catalyst (c). The value of the saturation magnetic moment of hercynite MNPs (Fig. 6a) was found to be ~ 41 emu/g. demonstrated the superparamagnetic properties of hercynite MNPS. The value of the saturation magnetic moment of the Hercynite@L-Methionine-Pd complex (Fig. 6b) is 26 emu/g as compared to the saturation magnetization of hercynite, which was found to be ~ 41 emu/g. This decrease in the saturation magnetization of Hercynite@L-Methionine-Pd complex is due to the successful immobilization of L-Methionine-Pd complex on the surface of hercynite MNPs. The value of the saturation magnetic moment of the recovered Hercynite@L-Methionine-Pd (Fig. 6c) is 24 emu/g, in which no significant change was observed as compaired to the fresh catalyst.



Fig. 6 VSM curve of hercynite (a) and Hercynite@L-Methionine-Pd(b) and recovered Hercynite@L-Methionine-Pd nanocatalyst (c) at room temperature.

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Catalytic studies

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After successful characterization of the synthezed Hercynite@L-Methionine-Pd, its catalytic activity was evaluated in C-C cross coupling reactions including Suzuki and Heck.

Intialy, the catalytic properties of Hercynite@L-Methionine-Pd were examined in Suzuki reaction.

In order to find the best conditions for Suzuki reaction, the coupling of iodobenzene (1 mmol) with phenylboronic acid (1 mmol) under different conditions was selected as the model reaction. Then, the effect of the different experimental parameters; including, the amount of the catalyst, solvent, base and also the effect of temperature on the selected model substrate were investigated. The results are summarized in Table 1.

In the first step, the influence of different amounts of the catalyst on the outcome of the reaction was studied, and it was revealed that the best yield was obtained in the presence of 0.1 mol% of Hercynite@L-Methionine-Pd. Meanwhile, in the absence of the catalyst, the reaction didn't proceed at all even after 48 hours (Table 1, entry 1). In the next step, the effects of the solvent, base and the reaction temperature were screened, and the best C-C coupling product was obtained in EtOH in the presence of K₂CO₃ as the most effective base under reflux conditions with the highest yield of the biphenyl product. According to the observed results, the optimal conditions for this reaction are: Hercynite@L-Methionine-Pd catalyst (0.1 mol%), K₂CO₃ (1.5 mmol) as base in the EtOH at reflux conditions (Table 1, entry 6).

 Table 1 Optimization of the reaction conditions for the C-C cross coupling of iodobenzene with phenylboronic acid.

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ידא איז	+		Base	e, solvent, <u>∆</u>	_/_\	
Entry	Catalyst (mol%)	Solvent	Base	Temperature (ºC)	Time (min)	Yield (%) ^a
1	-	EtOH	K_2CO_3	reflux	2 days	NR
2	0.020	EtOH	K_2CO_3	reflux	15	48
3	0.035	EtOH	K_2CO_3	reflux	15	76
4	0.050	EtOH	K_2CO_3	reflux	15	85
5	0.075	EtOH	K_2CO_3	reflux	15	92
6	0.100	EtOH	K_2CO_3	reflux	15	99
7	0.100	DMSO	K_2CO_3	110	15	96
8	0.100	DMF	K_2CO_3	110	15	91
9	0.100	PEG-400	K_2CO_3	110	15	95
10	0.100	H ₂ O	K_2CO_3	reflux	15	37
11	0.100	EtOH:H₂O	K_2CO_3	reflux	15	74
11		(1:1)				
12	0.100	Dioxane	K ₂ CO ₃	reflux	15	83

13	0.100	EtOH	КОН	reflux	View Artic	le Ontine
14	0.100	EtOH	NaOH	reflux	039/C9NJ 15	053258 81
15	0.100	EtOH	Na_2CO_3	reflux	15	91
16	0.100	EtOH	Et₃N	reflux	15	77
17	0.100	EtOH	-	reflux	15	NR
18	0.100	EtOH	K_2CO_3	25	15	NR
19	0.100	EtOH	K_2CO_3	50	15	53
20	0.100	EtOH	K_2CO_3	65	15	76
21	0.100	EtOH	K_2CO_3	70	15	88

^a Isolated yield.

^b Reaction conditions: aryl halide (1mmol), phenylboronic acid (1mmol), Hercynite@L-Methionine-Pd, base (1.5 mmol) and solvent (3mL).

After optimizing the reaction conditions, the catalytic effectiveness of Hercynite@L-Methionine-Pd MNPs was investigated in the Suzuki C-C cross-coupling reactions of a wide range of commercially available aryl halides with phenylboronic acid as phenylating source. The results are listed in (Table 2) in which the target products were afforded in moderate to excellent yields. The experimental results show that various ortho-, meta-, and parasubstituted aryl halides; including, aryl iodide, aryl bromides and aryl chlorides having both electron-withdrawing and electrondonating groups such as NO₂, NH₂, CN, CF₃, CH₃ and OCH₃ produced their corresponding derivatives in good to excellent yields. However, it is worth mentioning that the reaction time of the aryl halides with electron-donating groups on the aromatic ring was longer than aryl halides with electron-withdrawing groups. Due to the fact that the aryl halides are electrophilic partners in Suzuki reaction, they have been activated by electron-withdrawing (EWD) groups in the ortho or para positions, in oxidative addition step as compared to those with electron-donating groups ⁶⁵. Moreover, the Suzuki C-C cross-coupling of phenylboronic acid with aryl iodide and aryl bromides, is easier than those with aryl chlorides. Because the order of reactivity of the electrophilic partners in Suzuki coupling, based on the power of leaving groups, is: I >> Br > OTf >> Cl > F, the chloride electrophiles are the most nonreactive ones as they are reluctant to participate in oxidative addition ⁶⁶. In order to show the chemoselectivity of this new catalytic system, the reaction of 1bromo-4-chloro benzene was also investigated in which the bromide group showed more reactivity (Tables 2 entry 9). This selectivity allows to remain an active halide site for further functionalization.

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 Table 2 Catalytic Suzuki C-C coupling reaction in the presence of catalytic amounts of Hercynite@L-Methionine-Pd in EtOH at 80 °C.

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	×	B(OH) ₂	Hercynite@	DL-Mwthioni	ne-Pd ((cat)		
	X= CL Br L	T	K ₂ CC	0₃, EtOH, Ref	lux	R		,
Entry	Arvl halide	Product	Time (min)	Yield (%) ^a	TON	TOF (min ⁻¹)	Meltin	g point
					_	- ()	measured	literature
1			15	99	990	66	61-63	62-64 ⁶⁷
2	Me	Me	30	97	970	32.33	43-44	43-45 ⁶⁷
3	MeO	MeO	20	98	980	49	81-83	82-85 ⁶⁷
4	Br	$\bigcirc - \bigcirc \bigcirc$	30	93	930	31	62-64	62-64 ⁶⁷
5	Me	Me	25	93	930	37.2	43-45	43-45 ⁶⁷
6	NC Br		25	97	970	38.8	84-86	82-84 ⁶⁷
7	OMe	MeO	80	90	900	11.25	80-82	81-82 ⁶⁹
8	CF ₃	F ₃ C	90	84	840	9.33	26-27	27 ³⁸
9	CI	CI	30	92	920	30.66	72-73	70-72 ⁶⁸
10	O ₂ N Br	0 ₂ N	20	97	970	48.5	111-113	111-114 ⁶⁷
11	CI		75	87	870	11.6	67-68	62-64 ⁶⁷
12	O ₂ N CI	0 ₂ N-	60	92	920	15.33	111-112	111-113 ⁶⁸

^a Isolated yield.

^bReaction conditions: aryl halide (1mmol), Hercynite@L-Methionine-Pd (0.1 mol %), phenylboronic acid (1mmol) and K_2CO_3 (1.5 mmol) in EtOH at 80 °C (reflux conditions).

The catalytic cyclic mechanism for Suzuki reaction in the presence of Hercynite@L-Methionine-Pd is shown in the Scheme 2 based on previously reported mechanism⁵³.

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Scheme 2. Mechanism of the palladium-catalyzed Suzuki reaction.

In the next part of this research project, the catalytic activity of Hercynite@L-Methionine-Pd for the Heck reaction was investigated. For this purpose, the coupling of iodobenzene with butyl acrylate as olefin source was selected as the model reaction to optimize the reaction conditions. Then, the effect of various parameters was studied including amount of the catalyst, solvent, base and temperature on the reaction efficiency (Table 3). Initially, the effect of different amounts of the catalyst on the outcome of reaction was investigated. Among the various catalyst loadings (e.g., 0.025, 0.050, 0.075.0.100, 0.125 and 0.15 mol%), 0.125 mol% of the catalyst on the basis of Pd was selected as the most effective amount (Table 3, entry 5). Meanwhile, in the absence of the catalyst, the reaction didn't proceed at all even after 48 hours (Table 3, entry 1). Then, the influence of the solvent on the outcome of the reaction was studied. The obtained results revealed that PEG-400 is the most effective solvent for this type of coupling reaction. Subsequently, the effect of base and temperature was examined, the results revealed that the highest yield of the coupling product was obtained in the presence of K_2CO_3 as base at 120 °C. Eventually, PEG-400 at 120 °C in the presence of Hercynite@L-Methionine-Pd (0.125 mol%) was found to be the best choice for mentioned model reaction.

 Table 3 Optimization of reaction conditions for C-C coupling reaction of iodobenzene with butyl acrylate.

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	*	O Bu	Base, Sol	vent, ∆	Ĵ	0
Entry	Catalyst	Solvent	Paca	Temperature	Time	Yield
Entry	(mol%)	Solvent	Base	(°C)	(min)	(%)a
1	-	PEG-400	K_2CO_3	120	2 days	NR

2	0.025	PEG-400	K_2CO_3	120	45 View Artic	le Ontine
3	0.050	PEG-400	K_2CO_3	120 ^{I: 10.10}	39/C9N3 45	105325E 63
4	0.075	PEG-400	K_2CO_3	120	45	84
5	0.100	PEG-400	K_2CO_3	120	45	91
6	0.125	PEG-400	K_2CO_3	120	45	98
7	0.150	PEG-400	K_2CO_3	120	45	98
8	0.125	EtOH	K_2CO_3	120	45	79
9	0.125	H ₂ O	K_2CO_3	120	45	64
10	0.125	EtOH: H₂O	K_2CO_3	120	45	83
10		(1:1)				
11	0.125	DMSO	K_2CO_3	120	45	96
17	0.125	Solvent-	K_2CO_3	120	45	Trace
12		free				
13	0.125	PEG-400	Na ₂ CO ₃	120	45	94
12	0.125	PEG-400	КОН	120	45	43
13	0.125	PEG-400	NaOH	120	45	46
14	0.125	PEG-400	Et_3N	120	45	88
15	0.125	PEG-400	-	120	2 day	NR
16	0.125	PEG-400	K_2CO_3	r.t	45	NR
17	0.125	PEG-400	K_2CO_3	50	45	48
18	0.125	PEG-400	K_2CO_3	60	45	69
19	0.125	PEG-400	K_2CO_3	65	45	83
20	0.125	PEG-400	K ₂ CO ₃	70	45	91

^a Isolated yield

^b Reaction conditions: aryl halide (1mmol), Hercynite@L-Methionine-Pd, butyl acrylate (1.2 mmol), base (3 mmol), and solvent (2ml).

In order to investigate the scope and generality of this procedure, different electron-withdrawing or electron-donating groups, such as OCH₃, NO₂, NH₂, and CH₃ were selected to react with butyl acrylate under optimized reaction conditions. The results are summarized in Table 4. The experimental results show that various aryl halides; including, aryl iodide, aryl bromides and aryl chlorides having both electron-withdrawing and electron-donating groups (such as NO₂, NH₂, CN, CF₃, CH₃ and OCH₃) produced their corresponding derivatives in good to excellent yields. However, it is worth mentioning that the reaction time of the aryl halides with electrondonating groups on the aromatic ring was longer than aryl halides with electron-withdrawing groups due to the fact that oxidative addition is the most difficult step of the entire catalytic cycle 65. The rate of oxidative addition also depends on the chemical property of halides. As mentioned above, electron-withdrawing (EWD) groups on aryl halides increase their reactivity in oxidative addition step as compared to those with electron-donating groups ⁶⁶.

In order to show the chemoselectivity of this new catalytic system, the reaction of 1-bromo-4-chloro benzene was also investigated in which the bromide showed more reactivity (Tables 4 entry 8). This

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selectivity	allows	an	active	halide	site	to	remain	for	further
functionali									

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 Table 4 Coupling of aryl halides and butyl acrylate in the presence of catalytic amounts of Hercynite@L-Methionine-Pd.

		K O Hei	rcynite@L-Mwthi	ionine-Pd (cat)	\land	O Bu	
	X= CL Br L	- O Bu	K ₂ CO ₃ , PEG-40	00, 120 °C	Ī		0	
Entry	Aryl halide	product	Time (min)	Yield (%) ^a	TON	TOF (min ⁻¹)	Meltin	ig point
1		O Bu	45	98	784	52.266	Oil	Oil ⁷⁰
2	Me	Me O Bu	70	96	768	10.971	Oil	Oil ⁷⁰
3	MeO	MeO O Bu	50	93	744	14.88	Oil	Oil ⁷⁰
4	OMe	OMe O	180	91	728	4.044	Oil	Oil ⁷⁰
5	Br	O ^{Bu}	50	96	768	15.36	Oil	Oil ⁷⁰
6	Me	Me O	80	89	712	8.9	Oil	Oil ⁷⁰
7	NC	NC O	35	96	768	21.94	40-42	39-42 ⁷⁰
8	CI	CI O Bu	65	91	728	11.2	Oil	Oil ⁷⁰
9	O ₂ N Br	O ₂ N O	50	97	776	726	59-62	58-63 ⁷⁰
10	CI	O Bu	240	93	744	3.1	Oil	Oil ⁷⁰
11	O ₂ N CI	O ₂ N O	320	95	760	2.375	60-62	60-63 ⁷¹
12	NC	NC Bu	380	93	744	1.957	39-41	39-42 ⁷¹

^a Isolated yield.

 ^bReaction conditions: aryl halide (1mmol), Hercynite@L-Methionine-Pd (0.125 mol %) butyl acrylate (1.2 mmol) and K₂CO₃ (3

mmol) in PEG-400 at 120 °C.

The purposed mechanism for Heck cross coupling reaction in the

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presence of Hercynite@L-Methionine-Pd has been outlined in Scheme 3, based on the previously reported mechanism ^{72,73}.



Scheme 3. Mechanism of the palladium-catalyzed Heck reaction.

Recyclability of the catalyst

Recyclability of heterogeneous catalysts is an important advantage in industrial applications. Therefore, the recoverability and reproducibility of Hercynite@L-Methionine-Pd were explored in the synthesis of 1,1'-biphenyl (Fig. 7 series 1) and butyl cinnamate (Fig. 7 series 2). After the completion of the reaction, the Hercynite@L-Methionine-Pd catalyst was separated using an external magnet, washed with EtOAc and water and dried at 80 °C. Then, it was reused for the next run. As shown in Fig. 8, the recycling process was repeated for five times with a slight decrease in the activity of the catalyst.



Fig 7. Recyclability of Hercynite@L-Methionine-Pd in the synthesis of 1,1'-biphenyl (series 1) and butyl cinnamate (series 2).

In addition, to examine stability of this catalyst during organic reactins, the recycled catalyst has been characterized by ICP-OSE and SEM techniques. The SEM image of the recycled catalyst is shown in fig. 8. As found in the SEM images of Fig. 8, the morphology of the recovered Hercynite@L-Methionine-Pd is compairable with fresh catalyst, which indicates the structural stability of the catalyst after 5 consecutive cycles. In addition, the exact amount of Pd in the recovered Hercynite@L-Methionine-Pd, was obtained by ICP-OSE: $1.18 \times 10^{-3} \text{ mol}_{\text{view}} g_{\text{Article}}^{-1}$ These characterizations confirmed that the structure of recovered catalyst dose not change in morphology and content during coupling reactions.



Fig 8. SEM images of recovered Hercynite@L-Methionine-Pd nanocatalyst.

Hot filtration test

The heterogeneity of Hercynite@L-Methionine-Pd MNPs in the reaction mixture was studied using the hot filtration test. The hot filtration test was performed in Suzuki cross-coupling reaction in the synthesis of 1,1'-biphenyl under the optimal reaction conditions. After the half reaction time, the reaction was terminated and the corresponding product was obtained in 61 % of yield. Then, the reaction was repeated, and at the half time of the reaction, the catalyst was separated by magnetic separation from the reaction mixture, which was allowed to react further. Accordingly, we found that only a trace conversion (<3%) of the coupling reaction was observed upon heating of the catalyst-free solution for another half time of the reaction, which means that the described nanocatalyst is completely heterogeneous in the reaction media.

Comparison

In order to demonstrate the superiority of our catalyst to the other reported catalysts for the synthesis of 1,1'-biphenyl (Table 5 entry 1-9) and Butyl cinnamate (Table 5 entry 10-17) as the representative examples, they were compared to the best of the well-known data from the literature as outlined in the Table 5. As it can be seen in this Table, this new method was better than the other catalysts in terms of reaction conditions, time and yield factors.

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Entry	Substrate	Catalyst	Time (mine)	Yield (%) ^a	View Ref. Onlir
1	Phenylboronic acid	VO(IV)–MCM-41	720	100: 10.1	039/C9NJ05325 74
2	Phenylboronic acid	Zirconium ferrite MNPs	900	83	53
3	Phenylboronic acid	Pd@DCA-SBA	120	95	75
4	Phenylboronic acid	Fe ₃ O₄@SiO₂@L-arginine@Pd(0)	15	91	76
5	Phenylboronic acid	Fe ₃ O ₄ @Boehmite-NH ₂ -Coll NPs	30	95	77
6	Phenylboronic acid	Pd@DCA-MCM	120	94	78
7	Phenylboronic acid	MCM-Pd	1440	74	79
8	Phenylboronic acid	Boehmite@Tryptophan-Pd	30	98	2
9	Phenylboronic acid	Hercynite@L-Methionine-Pd	15	99	This work
10	Butyl acrylate	Pd-DABCO-γ-Fe ₂ O ₃	30	92	80
11	Butyl acrylate	Fe ₃ O ₄ /SiO ₂ -DTZ-Pd	30	92	81
12	Butyl acrylate	PdCl2	360	96	82
13	Butyl acrylate	Dibromobis(1-(4-Methoxyphenyl)-1H-imidazole)palladium(II)	1440	89	83
14	Butyl acrylate	[Pd(PPh ₃) ₂ Cl ₂]	720	85	84
15	Butyl acrylate	Pd(OAc)	1440	76	85
16	Butyl acrylate	Boehmite@Tryptophan-Pd	85	95	2
17	Butyl acrylate	Hercynite@L-Methionine-Pd	45	98	This work

Conclusions

 In this study, we described a simple strategy to immobilize Lmethionine-Pd complex on the surface of hercynite MNPs by covalent cross-linking. The structure and composition of the prepared Hercynite@L-Methionine-Pd MNPs were completely

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characterized by FT-IR, XRD, EDX, ICP, SEM, X-ray mapping, and TGA and VSM techniques. Moreover, the catalytic activity of this nanocomposite was investigated in Suzuki and Heck C-C cross-coupling reactions of aryl halides with phenylboronic acid as phenylating source and butyl acrylate as olefin source in EtOH and PEG-400 under green conditions. Therefore, high surface area, convenient recoverability and reusability for several times without any significant loss of catalyst activity, the use of a commercially available materials, eco-friendly procedure, operational simplicity, ease of separation by simple filtration, cheap and chemically stabile reagents, good reaction times, simple practical methodology and ease of use make the prepared catalyst a promising candidate for potential applications in some organic reactions.

Conflicts of interest

There are no conflicts to declare

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The first report of hercynite as a solid support, L-methionine-Pd complex supported on hercynite as highly efficient reusable nanocatalyst for C-C cross coupling reactions

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L-Methionine-Pd complex was covalently immobilized on the surface of hercynite (FeAl₂O₄) MNPs, and its catalytic properties has been studied in C-C coupling reactions.