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# Bentonite clay as an efficient substrate for the synthesis of the super stable and recoverable magnetic nanocomposite of palladium (Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd)

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#### **Keywords:**

Magnetic nanoparticles, Palladium, Bentonite clay, C-C coupling, Heterogenization, Green catalyst, Suzuki reaction

#### Abstract

Bentonite has a potential for the catalytic carrier because their surface and special structure are very suitable for supporting transition metals. This clay as a nontoxic, inexpensive, freely available and abundant natural mineral was used to synthesize magnetic nanocomposite of palladium as a super stable and recoverable green catalyst (Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd). The catalytic activity of this system was evaluated in the Suzuki cross-coupling reaction. Determination of novel nanoparticles structure was performed using FT- IR, XRD, VSM, TGA, and SEM–EDX spectral data. **Introduction** 

Since the beginning of history, soils play an effective rule in humane life. They are useful materials for many purposes such as constructing shelters, producing consumable goods, industrial and pharmaceutical applications [1-3]. There are different kinds of soil in nature, each having unique structure and characteristics such as texture, color, contents. Clays are the most important category of soils which are a class of inorganic layered compounds. Clay particles have a diameter of less than 0.002 mm. Among the minerals in clay, bentonite is one of the most important natural material that has many usages in industries such as bonding, plasticizing, and suspending.

The large surface area, mechanical properties, high thermal stability, and other unique properties have caused that bentonite widely applied in adsorbents and composites.[4] Bentonite consists of two silica tetrahedral sheets and one central alumina octahedral sheet. The structural formula of Bentonite is defined as  $R_x(H_2O)_4\{(Al_{2-x},Mg_x)_2[(Si,Al)_4O_{10}](OH)_2\}$  that R is the exchangeable cations of alkali and alkali-earth metals between the layers.[5] It has a cation-exchange capacity of about 70 to 110 meq/100 g of clay.[6] Schema of bentonite structure shown in Fig. 1.



Fig 1. Schema of bentonite structure with exchangeable cations.

Literature mining revealed that bentonite can absorb heavy metals such as Cd(II), Ni, Pb(II), and Co(II) from aqueous solution and wastes.[3, 7-9] Also Buxing and co-works showed that bentonite has very great potential in green chemical processes to absorbed palladium in the surface and make a stable composite.[10]

The main challenge in the industry is the design of efficient catalysts that are environmentally friendly and consistent with the principles of green chemistry.[11-13] According to the principles of green chemistry, a catalyst should not pollute the environment and have no degradation effects, therefore the use of heterogeneous catalysts that are easier to separate from the reaction media is more important than homogeneous catalysts. The toxicity of homogeneous catalysts, difficult

separation, and not using them more than once are problems of these catalysts.[14] Recently, to avoid these problems, a heterogeneous catalytic system has been extensively used in industrial and various synthetic reactions. The use of heterogeneous systems in reactions has been many advantages such as mild reaction conditions, the reusability of catalysts, straightforward experimental procedures, and minimal waste disposal.[15]

Today, many methods and system are used to prepare such catalysts. Among them, the use of a surface containing magnetic nanoparticles is a useful method, in which the catalyst can be separated by using an external magnetic field. The advantages of these catalysts can be summarized in minimizing changes in the activity, selectivity and, longer lifetimes than homogeneous catalysts.[16, 17] The magnetic nanoparticles surface may be synthesized using different methods, such as (a) covering the surface with oxides, carbon, polymer, or metallic layers; (b) the non-covalent approach with polymers or surfactants; or (c) the covalent approach between hydroxyl groups of the nanoparticles surface and anchoring agents such as carboxylic acid, phosphoric acid, and dopamine derivatives.[17, 18]

The carbon-carbon cross-coupling reactions are an important class of reactions which accepted in the synthesis of natural products, agrochemical, pharmaceuticals and bioinorganic materials. This method is also utilized to the selective construction of biaryls.[19] The usefulness of the Suzuki reaction is attributed to the non-toxicity boron compounds, the convenient replacement of boron by other groups and the ability to use it in environmentally friendly solvents.[20-23] In recent years, many improvements have been made in this field and known as the Suzuki-Miyaura cross-coupling reaction.[24, 25] Palladium is an expensive metal that is not economically useful as a homogeneous catalyst because some of it is wasted in the separation step. To resolve this problem, the use of heterogeneous palladium catalysts such as palladium complexes immobilized on polymer, carbon, silica, alumina, metal oxides and other inorganic supports have been recommended.[26-37] In spite of the successful processes in this area, there are still some requests for development of new protocols in this field for C-C coupling which complies with the following conditions: a low quantity of catalyst, highly efficient in terms of reactivity and selectivity, ease separation of catalyst, reuse of it without reducing its activity and high efficiency of products.

According to the above-mentioned points, we decided to synthesize an efficient palladium magnetic composite by using bentonite clay. In this system, we used bentonite as a ligand for the

heterogenization of palladium chloride on  $Fe_3O_4$  nanoparticles surface as a novel, inexpensive, recoverable, high temperature stable, and green catalyst ( $Fe_3O_4$ /bentonite-Pd). The TGA analysis of this catalyst shows that it has great stability, keeping its nature at temperatures over 600 °C. Also, it exhibited an excellent catalytic activity in the Suzuki cross-coupling reactions. The structure of catalyst was characterized systematically by different techniques such as FT-IR, ICP, SEM-EDX, XRD, VSM, and TGA.



### **Experimental section**

#### Material

All solvents and reagents were directly used in analytical grade purity without further purification. All experiments were performed using deionized water.

#### Characterization

FT-IR spectra were recorded on a commercial spectrophotometer (Bruker Tensor 27 FT -IR). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 Ultrashield NMR Magnet (400 MHz for <sup>1</sup>H NMR) with TMS as the internal standard. Powder X-ray diffraction (XRD) spectra were recorded at room temperature with a Philips X-Pert 1710 diffractometer using Co K $\alpha$ ( $\lambda$ =1.78897 Å) at a voltage of 40 Kv and a current of 40 mA and data were collected from 10° to 90° (20) with a scan speed of 0.02° s. The morphology of the catalyst was studied using scanning electron microscopy (SEM; Philips XL 30 and S-4160) with coated gold equipped with dispersive X-ray spectroscopy capability. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a thermal analyzer with a heating rate of 20°C min in a temperature range of 25–1100°C under flowing compressed nitrogen. The magnetic property of the catalyst was measured with a vibrating sample magnetometer (VSM).

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/Bentonite

Bentonite (1 g) was dispersed in 50 ml of deionized water via adequate ultrasonic. The solution was then stirred for 1h and then the solution was added to 50 ml of distilled water containing FeCl<sub>2</sub>·4H<sub>2</sub>O (0.8457 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (2.2992 g). The mixture was stirred under N<sub>2</sub> atmosphere at 80°C for 0.5 h. Then, 25 ml of 25% (W/W) NH<sub>3</sub>·H<sub>2</sub>O was rapidly injected into the reaction mixture and stirred under N<sub>2</sub> for another 1h. The obtained magnetic composite was washed three times with hot water and separated by an external magnet and was dried under vacuum at 70°C.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd

0.5 g of Fe<sub>3</sub>O<sub>4</sub>/bentonite composite (which was previously prepared) was added to a mixture of 105 mg of palladium (II) chloride and 50 mL solvent (H<sub>2</sub>O/MeOH 1:1). The mixture was continuously stirred for 24 h at room temperature. The composite material was separated by an external magnet and washed thoroughly with distilled water and was dried under vacuum at 70  $^{\circ}$  C for 5 h to give the catalyst Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd.

#### General procedure for the Suzuki–Miyaura coupling reactions

Catalyst (10 mg), arylhalide (1.0 mmol, 1 equiv.), phenylboronic acid (0.14 g, 1.2 mmol, 1.2 equiv.), potassium carbonate (0.26 g, 2.0 mmol) and a solution of 10 mL of EtOH/H<sub>2</sub>O (v/v = 1/1) were mixed in a round bottom flask. The mixture was vigorously stirred at 80 °C for 20 min (Scheme 2). The reaction was monitored through Thin Layer Chromatography (TLC). When the reaction completed, the catalyst was recovered with an external magnet and product was extracted with dichloromethane ( $2 \times 30$  ml). Then the organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The products were purified using a short column of silica gel with eluted (silica gel, n-hexane).

**2-Methoxy-biphenyl** (Table 2, entry 4). Yield 65%. A colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (d, 2H, J=7.39 Hz), 7.52 (t, 2H, J=7.39 Hz), 7.44-7.41 (m, 3H), 7.14 (t, 1H, J=7.3 Hz), 7.08 (d, 1H, J=8.2 Hz), 3.9 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 55.64, 111.35, 120.98, 127.07, 128.14, 128.78, 129.71, 130.84, 131.04, 138.70, 156.59.

**4-Methoxy-biphenyl** (Table 2, entry 5). Yield 90%. Mp 85-88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62-7.55 (m, 4H), 7.46 (t, 2H, J=7.7 Hz), 7.35 (t, 1H, J=7.3 Hz), 7.02 (d, 2H, J=8.5 Hz), 3.91 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 55.37, 114.24, 126.70, 126.78, 128.19, 128.77, 133.79, 140.86, and 159.18.

**1-Phenyl naphthalene** (Table 2, entry 7). Yield 75%. A colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, 2H, J= 8. 8 Hz), 7.78 (d, 1H, J=9.0, 1.6 Hz), 7.47-7.39 (m, 6H), 7.37-7.33 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 125.58, 125.96, 126.22, 127.13, 127.42, 127.83, 128.45, 128.47, 129.05, 130.26, 131.80, 133.99, 140.43, 140.94.

**2'-fluoro-1,1':4',1''-terphenyl** (Table 2, entry 8). Yield, 60%. Mp 152-154 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69-7.65 (m, 4H), 7.59-7.41 (m, 9H).

**4-Acetylbiphenyl** (Table 2, entry 9). Yield 90%. Mp 116-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, 2H, J= 8.5 Hz), 7.71 (d, 2H, J=8.01 Hz), 7.65 (d, 2H, J=6.7 Hz), 7.50 (t, 2H, J=7.6 Hz), 7.43 (t, 1H, J=7.3 Hz), 2.67 (s, 3H, CH<sub>3</sub>).

**4-Methyl-biphenyl** (Table 2, entry 10). Yield 95%. Mp 46-47 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (dd, 2H, J= 8.0, 0.8 Hz), 7.56 (dd, 2H, J=8.0, 1.6 Hz), 7.48 (t, 2H, J=7.8 Hz), 7.38 (t, 1H, J=7.4 Hz), 7.31 (d, 2H, J=7.9 Hz), 2.45 (s, 3H, CH<sub>3</sub>).

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**4-Nitro-biphenyl** (Table 2, entry 11). Yield 78%. Mp 111-113 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, 2H, J= 8.7 Hz), 7.76 (d, 2H, J=8.7 Hz), 7.65 (d, 2H, J=7.45 Hz), 7.55-7.46 (m, 3H)

**4-Cyano-biphenyl** (Table 2, entry 13). Yield 79%. Mp 84-86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (m, 4H, J= 18.0 Hz), 7.62 (d, 2H, J=8.0, 7.11 Hz), 7.52 (t, 2H, J=6.8 Hz), 7.46 (d, 1H, J=7.1 Hz).

#### **Results and Discussion**

#### FT-IR Spectra

XC

Figure 2 shows the FT-IR spectra of (a) bentonite, (b)  $Fe_3O_4$ /bentonite, and (c)  $Fe_3O_4$ /bentonite-Pd composite. The FT-IR spectrum of bentonite exhibits stretching bands at 3627 and 3440 cm<sup>-1</sup> for O–H and hydrogen binding of H<sub>2</sub>O molecules. Absorption bands of H–O–H deformation appear at 1668 and 1644 cm<sup>-1</sup>. Absorption band of Si–O–Si appears at 1038 cm<sup>-1</sup>. Absorption band of 796 cm<sup>-1</sup> is attributed to the Si–O stretching of quartz and silica and the band at 522 cm<sup>-1</sup> is due to the Al–O–Si deformation. In the FT-IR of Fe<sub>3</sub>O<sub>4</sub>/bentonite, (Fig. 2b) the absorption band at 566 cm<sup>-1</sup> is related to the Fe–O stretching vibration of the bare magnetic nanoparticles.[38] Fig. 2(c) exhibits the IR spectrum of the final catalyst indicating the presence of Pd on Fe<sub>3</sub>O<sub>4</sub>/bentonite. As you can see, all absorbing bands have shifted to lower frequencies, and this confirms that palladium metal was placed on the magnetic composite. For example, the stretching frequency of hydroxyl group shifted to a lower frequency at 3417 cm<sup>-1</sup>. This shift approves that the OH group was coordinated to the palladium ion.



Fig 2. FT-IR spectra of (a) bentonite, (b) Fe<sub>3</sub>O<sub>4</sub>/bentonite, and (c) Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd composite.

#### **SEM-EDX Analyze**

The surface morphology of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd composite was analyzed using SEM and TEM technique (Fig 3). According to the images obtained from the catalyst levels, spherical nanoparticles of Pd and Fe<sub>3</sub>O<sub>4</sub> have successfully been deposited on surfaces of bentonite. Also, these images indicate that nanoparticles size is between 30-50 nm. Transmission electron microscopy (TEM) confirmed the formation of single-phase Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the surface of bentonite with spherical morphology (Fig 3b).



Fig 3. SEM image of Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd (a), and TEM image of Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd (b).



Fig 4. EDX analyze of Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd.

EDX is a qualitative technique used to prove the presence of elements in a catalyst. EDX spectrum of  $Fe_3O_4$ /bentonite-Pd composite is shown in Fig.4. This spectrum confirms that several elements such as Fe, Pd, Si, Al, O, and Mg are present in the catalyst. The analyses also confirm that Pd was coated in the catalyst structure.

#### Vibrating Sample Magnetometry analyze

The magnetic property of the catalyst was determined using a vibrating sample magnetometer (Lake Shore VSM7410) from -8000 Oe to +8000 Oe at room temperature. Bare nanocrystals of Fe<sub>3</sub>O<sub>4</sub> have a high saturation magnetization of 73.7 emu.gr<sup>-1</sup> which decreases to 32 emu.g<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd (Fig 5).[16] This magnitude of magnetization indicates that this nanocatalyst still has a high magnetic permeability and can be separated from the reaction mixture by an external magnet.



Fig 5. VSM curve of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd composite.

#### **XRD** pattern analyze

The XRD patterns of Fe<sub>3</sub>O<sub>4</sub>/bentonite similar diffraction peaks at around  $2\theta = 30.06^{\circ}$ ,  $36^{\circ}$ ,  $44.01^{\circ}$ ,  $54.70^{\circ}$ ,  $58.30^{\circ}$ ,  $64.28^{\circ}$ , and  $74.05^{\circ}$  which relate to the seven crystal faces (111), (220), (311), (400), (422), (511) and (440) respectively. These peaks are completely compatible with the standard pattern for crystalline magnetite (Fe<sub>3</sub>O<sub>4</sub>) with inverse spherical structure.[39] The six peaks of Fe<sub>3</sub>O<sub>4</sub>/bentonite can also be seen in the XRD pattern of the synthesized Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd. This comparison shows that the final structure of catalyst does not have two different phases, and the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles at this stage are pure and have a spinel structure. Also, the observed diffraction peaks in Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd at  $2\theta = 40$ , 46.5 and 68 are related to two faces (111), (200) and (220) respectively. These peaks are well suited to Pd<sup>0</sup>, which has been achieved by the reduction of Pd<sup>2+</sup> cations in methanol as solvent.[40, 41]



Fig 6. The XRD patterns of  $Fe_3O_4$ /bentonite (a) and  $Fe_3O_4$ /bentonite-Pd (b).

The thermogravimetric analysis (TGA) technique was used for measuring the sustainability of  $Fe_3O_4$ /bentonite-Pd, and was recorded by heating the sample at a rate of 10 °C min<sup>-1</sup>. As shown in Fig. 7, the endothermic peak at lower temperatures (lower than 110 °C) can be attributed to desorption of physically absorbed water on the surface of bentonite and  $Fe_3O_4$ . This analysis indicates that the 0.86% weight loss in the range of 400-600 °C can be attributed to the removal of water.[42] Therefore, this composite is stable at 600 °C, and according to this analysis, the  $Fe_3O_4$ /bentonite-Pd is a high-temperature-stable catalyst. The amount of palladium metal deposited onto the Fe<sub>3</sub>O<sub>4</sub>/bentonite was measured by induced coupled plasma (ICP) analysis, and the amount of Pd metal per gram of catalyst was determined to be 0.014 g (0.14 mmol g<sup>-1</sup>). Also, the ICP of the reused catalyst and hot filtration test were investigated and the results showed no change in the amount of palladium loaded on the catalyst surface after the reaction. These results confirm the true heterogeneity of nanocatalyst.



Fig 7. The TGA spectra of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd

#### **Catalytic activity**

The catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd was appraised in the C–C coupling reaction of aryl halides with phenylboronic acid. The coupling reaction of phenylboronic acid and iodobenzene was used to optimize conditions and the results are summarized in Table 1. Our observations showed that the reaction was not carried out in the absence of catalyst in the following conditions: phenylboronic acid (1 mmol, 0.122 g), iodobenzene (1 mmol, 0.204 g) and 2 mmol (0.276 g) potassium carbonate as base in EtOH/H<sub>2</sub>O (8 mL, 1:1) at 50 °C under an air atmosphere for 20 min (Table 1, entry 1). This result confirmed that the catalyst plays a vital role in this reaction (Table 1, entry 2). Then we examined the effect of temperature on the reaction. The best yields were obtained at 70 ° C (Table 1, entry 3). Several solvent systems were also examined and the best reaction efficiency (98% yield) was obtained in EtOH/ $H_2O$  (1:1). (Table 1, entries 3-6). Several bases such as KOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and CaCO<sub>3</sub> were used in the reaction and K<sub>2</sub>CO<sub>3</sub> had the best performance (Table 1, entries 3 and 9). In the next section, the reaction was performed in the presence of various amounts of catalyst 5, 7 and 10 mg, which the best yield was obtained when 10 mg of catalyst was used (Table 1, entries10-12). When the reaction was carried out in the presence of bentonite,  $Fe_3O_4$ , and  $Fe_3O_4$ /bentonite as catalysts, the yield of product was 0, 8 and 5% respectively (Table 1, entries 13-15).

Entry	Catalyst	Catalyst (mg)	Base (eq)	Solvent	Temp (°C)	Yield <sup>b</sup> %	
1	-	-	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	50	0	
2	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	50	84	
3	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	98	
4	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	70	10	
5	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 2:1	70	98	
6	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:2	70	56	
7	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	K <sub>2</sub> CO <sub>3</sub>	Acetone/H <sub>2</sub> O 1:1	70	0	
8	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	КОН	EtOH/H <sub>2</sub> O 1:1	70	45	
9	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	Na <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	90	
10	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	10	Ca <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	10	
11	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	5	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	20	
12	Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	7	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	52	
13	bentonite	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	0	
14	Fe <sub>3</sub> 04	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	8	
15	Fe <sub>3</sub> 0 <sub>4</sub> - bentonite	10	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O 1:1	70	5	

**Table 1.** Investigation of the optimal condition of Suzuki reaction in the presence of different catalyst and condition.<sup>a</sup>

<sup>a</sup> Reaction condition: Iodobenzene 1 mmol, phenylboronic acid 1 mmol, base 2 mmol, catalyst, solvent (8 mL), and under air atmosphere for 20 min. <sup>b</sup> Isolated yield.

Capability and efficiency of  $Fe_3O_4$ /bentonite-Pd were investigated in Suzuki reaction by using different aryl halides under optimized conditions. A variety of aryl halides were subjected to optimal conditions, and the results are shown in Table 2.



Catalyst: Fe<sub>3</sub>O<sub>4</sub>/Bentonite -Pd

Scheme 2. Optimize condition for C-C coupling of various aryl halides



**Table 2.** C-Coupling of various aryl halides in the presence of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd under optimal condition.<sup>a</sup>

<sup>a</sup> Reaction condition: 1 mmol of aryl halide, 1 mmol phenylboronic acid, 2 mmol  $K_2CO_3$  in 8 ml solvent (EtOH/H<sub>2</sub>O 1:1), and in the presence of 10 mg Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd at 70 °C for 20 min. <sup>b</sup> Isolated yield.

All products were known and characterized by melting point (mp), <sup>1</sup>H and <sup>13</sup>C NMR spectral data. These data are consistent with what is reported in the literature for these compounds.[43-49]

The difference of this catalyst with some catalysts used previously for the reaction of iodobenzene with phenylboronic acid is shown in Table 3. Also, all of the catalysts compared base on the turnover number (TON) and Turnover frequency (TOF) factors, that results show high TON and TOF factor for Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd with comparing to other catalysts. Efficient reusability, easy separation and short reaction time are advantages of the new catalyst.

**Table 3.** A comparison between the Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd and a number of catalysts which were previously used in the Suzuki reaction.

Catalyst	mol% Catalyst	Temp. (°C)	Time	Yield (%) <sup>a</sup>	TON <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>	[Ref]
NHC- PdCl <sub>2</sub> species	0.40	60	24 h	99	24750	1031	[50]
Fe <sub>3</sub> O <sub>4</sub> @EDTA-Pd <sup>2+</sup>	0.56	80	3 h	94	16785	5595	[16]
PdNPs/P. a. kurdicagum	0.10	60	15 min	95	95000	380000	[51]
MNP@PAMPS- Pd(II)	0.7	80	30 min	99	14143	28286	[52]
Fe <sub>3</sub> O <sub>4</sub> /bentonite-Pd	0.14	70	20 min	95	67857	203571	Present work

<sup>a</sup> Isolated yield; average of two runs.

<sup>b</sup> Turnover number: moles of aryl halide converted per mole of Pd.

<sup>c</sup> Turnover frequency.

To study the longevity and activity of the catalyst, it was separated from the reaction medium by an external magnet and used up to 5 times in the Suzuki reaction, and it was found that it still maintains its efficiency and can respond well (Fig. 8).



**Fig 8.** Reusability of Fe<sub>3</sub>O<sub>4</sub>/bentonite-Pd in the model reaction, (a) Reaction environment before catalyst isolation, (b) Catalyst adsorbed with an external magnet after completion of the reaction.

Pd leaching during the reaction process was scanned by ICP of recycled catalyst. The results didn't show any change in Pd amount in the structure of catalyst after recovering from the reaction mixture. The XRD patterns of the recycled catalyst after Suzuki model reaction is shown in Fig 9. These XRD patterns exhibit that the catalyst structure has not changed after the reaction.



Fig 9. XRD patterns of nanocatalyst after using in the reaction mixture

### Conclusions

In conclusion, in this study bentonite was used as a new and efficient substrate for heterogenization of palladium on the surface of magnetic nanoparticles. It is a super-stable composite in high temperature that can be used in the C-C coupling reactions. The catalytic activity of this nanocomposite was tested in the Suzuki cross-coupling reaction. The advantages of this catalyst include the use of a nanocomposite that meets the principles of green chemistry and avoids the use of environmental pollutants

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Acceletics

# Bentonite clay as an efficient substrate for the synthesis of super stable and recoverable magnetic nanocomposite of palladium (Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd)

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Bentonite as a nontoxic, inexpensive, free available and abundant natural clay was used to synthesize magnetic nanocomposite of palladium as a super stable and recoverable green catalyst (Fe<sub>3</sub>O<sub>4</sub>/Bentonite-Pd).

