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# Mesoporous palladium-copper ferrites as highly efficient and magnetically separable catalysts for Suzuki coupling reaction

Jinhui Tong <sup>[a, b]</sup>\*, Lingdi Su <sup>[a, b]</sup>, Lili Bo <sup>[c]</sup>, Xiaodong Cai <sup>[a, b]</sup>, Qianping Zhang <sup>[a, b]</sup>, Qizhao Wang <sup>[a, b]</sup>

- <sup>[a]</sup> Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, PR China.
- <sup>[b]</sup> Key Laboratory of Gansu Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China.

<sup>[c]</sup> College of Science, Gansu Agricultural University, Lanzhou 730070, P. R. China.

\*Corresponding author Fax: (+) 86-931-7971533; e-mail: jinhuitong@126.com (Jinhui Tong)

### **Graphical abstract**

### **Highlights**

- Mesoporous Cu-Pd ferrites were prepared by a facile, mild and environment-friendly route
- The catalysts have shown great efficiencies in Suzuki coupling reaction and up to  $36.9 \times 10^3$  h<sup>-1</sup> TOF can be obtained.
- The catalyst can be magnetically separated easily and have shown prominent recyclability.

#### Abstract

Mesoporous Cu-Pd ferrites were prepared by using MCM-41 and SBA-15 mesoporous molecular sieves as hard templates and well characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), ICP-atomic emission

spectroscopy, N<sub>2</sub> adsorption-desorption and X-ray photoelectric spectroscopy (XPS). Compared with samples prepared by the sol-gel auto-combustion methods, the as-prepared mesoporous ferrites have shown uniform pore size and much higher specific surface areas. The samples showed a remarkably high activity in connection with the Suzuki coupling reaction, especially  $Cu_{0.99}Pd_{0.01}Fe_2O_4$  prepared by using MCM-41 as template obtained an excellent TOF as high as  $36.9 \times 10^3$  h<sup>-1</sup> and no obvious decrease in the activity was observed after ten consecutive runs.

**Keywords:** A. Magnetic materials, B. Chemical synthesis, B. Magnetic properties, C. Transmission electron microscopy, D. Catalytic properties

### **1. Introduction**

The Suzuki coupling reaction is one of the most important reactions in processes of forming carbon-carbon bonds <sup>[1-4]</sup>, especially for the preparation of biaryls <sup>[5-8]</sup>. Generally, the Suzuki coupling reactions are catalyzed by homogeneous Pd-containing catalysts <sup>[9-11]</sup>. However, separation of the expensive catalyst is often problematic in these homogeneous systems. Moreover, aggregation and precipitation of palladium metal granules in the homogeneous systems always leads to the loss of activity of the catalysts. Therefore, heterogeneous catalysts are highly desirable, especially in large-scale synthesis, from both environmental and economic aspects.

A most important strategy to find catalysts is supporting the homogeneous one on a substrate material, such as Pd (II)-Schiff base complex supported by multi-walled carbon nanotubes <sup>[12]</sup>, Pd catalysts supported by functionalized mesoporous SBA-15 <sup>[13]</sup>, silica <sup>[14]</sup> and terpolymers <sup>[15]</sup>, etc. Recently, magnetic nanoparticles (MNPs)

supports, especially spinel ferrites have attracted much attention because the magnetic catalysts can be simply separated by applying external magnetic fields. Several magnetic ferrites have been used as supports for palladium nanoparticles, such as copper ferrite, zinc ferrite and cobalt ferrite <sup>[16-19]</sup>. Although the catalysts have shown high catalytic activities and excellent recyclabilities, Pd nanoparticles may leach unavoidably during the reaction and separation processes for such supported catalysts prepared relying on re-impregnating methods. Copper ferrite nanoparticles have also been widely used in catalytic and magnetic fields <sup>[19-23]</sup>. However, to the best of our knowledge, no Cu-Pd ferrite solid solutions have been used as catalysts for the Suzuki coupling reaction.

In this work, we prepared mesoporous Pd-doped copper ferrites with high specific surface areas using molecular sieves as templates. The synthesized materials have shown prominent catalytic activities and recyclabilities in connection with the Suzuki coupling reaction.

### 2. Experimental

#### 2.1. Materials and equipments

All chemicals were of analytical grade and used without further purification. XRD patterns of the synthesized materials were collected using a PANalytical X<sup>'</sup> Pert Pro diffractometer with Cu Kα radiation. TEM micrographs were obtained using a Hitachi H-600 microscope. BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. The Pd content was determined by inductively coupled plasma (ICP) on a Perkin-Elmer ICP/6500

atomic emission spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Mercury 400 MHz nuclear magnetic resonance instrument.

### 2.2. Synthesis of the samples

Mesoporous spinel Cu-Pd ferrite was synthesized according to the route reported in the literature <sup>[24]</sup> as follows: 2.5 g of the nitrate salts in stoichiometric proportion were pre-mixed together with 1.0 g of the selected mesoporous silica powder and ground in an agate mortar in the presence of 10 ml of n-hexane to yield a homogeneous mixture. The resulting mixture was subsequently dispersed in 30 ml of n-hexane and stirred overnight under reflux at 70 °C. After cooling, the solid products were recovered by filtration, dried in air at 70 °C and then calcined at 600 °C for 5 h. Finally, the silica template was selectively removed by treating the powders three times with NaOH (2 M, 24 h at room temperature). Cu<sub>0.99</sub>Pd<sub>0.01</sub>Fe<sub>2</sub>O<sub>4</sub> was prepared by using SBA-15 and MCM-41 as templates and designated as **CPFO-S** and **CPFO-M** respectively. For comparison, solid Cu<sub>0.995</sub>Pd<sub>0.005</sub>Fe<sub>2</sub>O<sub>4</sub>, Cu<sub>0.99</sub>Pd<sub>0.01</sub>Fe<sub>2</sub>O<sub>4</sub> and Cu<sub>0.98</sub>Pd<sub>0.02</sub>Fe<sub>2</sub>O<sub>4</sub> ferrite nano-powders were synthesized according to the sol-gel auto-combustion route described in our previous work <sup>[25]</sup> and designated as **CPFO-A0, CPFO-A1** respectively.

### 2.3. Suzuki coupling reaction process

All Suzuki coupling reactions were carried out in a 10 mL round bottom flask equipped with a reflux condenser. In a typical experiment, 0.5 mmol of aryl halide, 0.6 mmol of phenylboronic acid, 1.0 mmol of base and catalyst, 1.0 mL solvents were added to the flask. The resulting mixture was stirred in an oil bath at the specified

temperature for desired time. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by external magnet and washed with ethanol. The reaction mixture was diluted with water and extracted with ethyl acetate for three times. The organic layers were combined, dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the pure products. The identities of the products were confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

### 3. Results and discussion



#### 3.1. Characterization of the samples

Fig. 1. The XRD patterns of the samples

The XRD patterns of the samples are shown in **Fig. 1**, which are consistent with the standard pattern of face-centered cubic CuFe<sub>2</sub>O<sub>4</sub> (JCPDS NO.34-0425)<sup>[26, 27]</sup>. The eleven peaks at  $18.3^{\circ}$ ,  $29.8^{\circ}$ ,  $34.6^{\circ}$ ,  $35.9^{\circ}$ ,  $37.1^{\circ}$ ,  $41.6^{\circ}$ ,  $43.8^{\circ}$ ,  $58.0^{\circ}$ ,  $62.0^{\circ}$ ,  $63.8^{\circ}$  and  $74.7^{\circ}$  can be ascribed to the reflection of (101), (112), (103), (211), (202), (004), (220), (321), (224), (400) and (413) diffractions of CuFe<sub>2</sub>O<sub>4</sub>. The diffraction peaks in

Pd-doped samples were shifted  $0.02-0.08^{\circ}$  to lower 20 values as compared to the un-doped samples. This implies that Pd was doped in the lattice of CuFe<sub>2</sub>O<sub>4</sub> and formed ferrite solid solutions.



Fig. 2. The TEM images of a) MCM-41; b) SBA-15; c) CPFO-M; d) CPFO-S;

#### e) CPFO-A



Fig. 3. The EDX images of a) CPFO-M based on the image c in Fig. 2; b) CPFO-S based on the image d in Fig. 2

The morphologies of the samples and the two template molecular sieves were characterized by TEM (Fig. 2). TEM images of MCM-41 and SBA-15 (Fig. 2a, Fig.

**2b**) show highly ordered mesoporous structures, which are in agreement with the literature <sup>[28, 29]</sup>. **Fig. 2c** and **Fig. 2d** show representative TEM images of **CPFO-M** and **CPFO-S** obtained from the replication of MCM-41 and SBA-15 respectively. The two replicas clearly present extended domains of the ordered 3D pore structure. **Fig. 2e** is a representative TEM image of the solid samples **CPFO-A0**, **CPFO-A** and **CPFO-A1**. The three samples show an irregular morphology and the particle size distribution is broad (10-50 nm), concentrated in 25-30 nm primarily.

The EDX characteristics of CPFO-M and CPFO-S based on the corresponding TEM images in **Fig. 2** have shown in **Fig. 3**. The results confirmed the occurrence of homogeneous distributions of Cu, Fe, Pd, O and trace of residual Si.



Fig. **4.** Porous textures of the samples (a) The nitrogen adsorption-desorption isotherms and (b) pore size distribution curves of the samples

Fig. **4** presents the nitrogen adsorption-desorption isotherms and corresponding pore size distribution plots of the as-prepared samples. Those of the samples **CPFO-A0** and **CPFO-A1** are similar with that of the sample **CPFO-A**. So they are not presented tediously. The BET surface area, pore volumes and pore diameters of the samples are listed in **Table 1**. The N<sub>2</sub> adsorption-desorption isotherms of the

samples (**Fig. 4a**) exhibit typical type IV behavior with an H3-type hysteresis loop according to the IUPAC classifications indicating that all the samples have porous structure. The pore size distributions plots of the samples **CPFO-S** and **CPFO-M** indicate narrow mesopores distributions of ~7.7 nm and ~3.6 nm respectively, while that of the sample **CPFO-A** indicates broad piled pores distributions of ~14 nm (**Fig. 4b**). The results have shown that the sample **CPFO-M** possess the highest BET surface areas of 167.2 m<sup>2</sup>·g<sup>-1</sup> and the smallest pore size of 3.6 nm. Pd contents of the samples measured by ICP–atomic emission spectroscopy are also listed in **Table 1**. As can be seen that **CPFO-M** contains the lowest Pd content, only 0.14 wt.%.

Fig. **5** shows the X-ray photoelectron spectroscopy (XPS) data for the catalyst. The wide spectra (**Fig. 5a**) of the catalysts reveal the predominant presence of copper, iron, oxygen, and carbon. The surface content of Pd was examined by high-resolution X-ray photoelectron spectroscopy (XPS). As shown in **Fig. 5b**, The Pd-3d spectra revealed a negligible surface palladium content on the catalysts (below the detection limit). We have noticed the fact that XPS signals were noisy and tried to increase the number of scans, which however did not lead to any improvement unless for those samples with higher elemental contents.



Fig. 5. XPS spectra for the samples: (a) wide spectra, (b) Pd 3d

#### 3.2. Catalysis tests

The catalytic performances of the as-prepared catalysts were evaluated in the Suzuki coupling reaction of 4-nitro-bromobenzene and phenylboronic acid and the results have been listed in Table 2. The results have shown that no reaction occurred in the absence of catalyst (entry 1). It is clear that the mesoporous samples have shown much higher catalytic activities than the solid ones and the ferrites supported Pd catalysts reported in the references <sup>[17, 30]</sup> probably due to their higher surface areas and mesoporous structures (entries 2-6). Especially, the catalyst CPFO-M has shown the highest activity and as high as 98% yield and a  $24.83 \times 10^3$  h<sup>-1</sup> TOF can be obtained after 0.5 h reaction at 70 °C (entry 4). As for the solid catalysts, they have shown different activities in the coupling reaction between 4-methoxybromobenzene and 4-chlorophenylboronic acid mainly due to their different Pd contents since they have similar structures. The results have shown that the yield of the product increased with increasing Pd content (entries 7-9). The catalyst CPFO-A1, which contained the highest Pd content of 0.87 wt%, has obtained the highest yield (97%) and the lowest TOF (170 h<sup>-1</sup>) (entry 9). Based on above facts, **CPFO-M** was chosen as the catalyst to

optimize the reaction conditions.

#### 3.3. Optimization of the Reaction Conditions

The Suzuki coupling reaction of 4-nitrobromobenzene and phenylboronic acid was selected as the model reaction to optimize the reaction conditions and the results are listed in **Table 3**. Among the investigated solvents, mixture of ethanol and water with 1:1 volume ratio was found the best one and the highest yield (about 98%) was obtained (entry 4). The base is considered to be crucial in the Suzuki-coupling reaction. Among the investigated bases,  $K_2CO_3$  was found to be the top one under our reaction conditions and the highest yields about 98% was obtained (entry 4). The effect of the catalyst amount was also investigated and the results have shown that the yield increased from 97% to 99% while the TOF decreased from 36.9×10<sup>3</sup> to 18.8×10<sup>3</sup> h<sup>-1</sup> when the catalyst amount increased from 2.0 mg to 4.0 mg (entries 4, 10, 11). In pursuit of higher TOF, 2.0 mg catalyst was employed in the following investigation.

#### 3.4. Extension of the Substrate Scope

Based on above investigations, the general applicability of the catalyst **CPFO-M** in the coupling of various aryl halides and arylboronic acids was investigated under the optimized conditions. The results are summarized in **Table 4**. As can be seen, the catalyst has shown prominent catalytic activities for aryl iodides and bromides including not only activated ones with electron-withdrawing substituents (entries 3, 4), but also deactivated ones with electron-donating substituents (entries 5-14), and

moderate yields (59-99%) and high TOF of up to  $36.9 \times 10^3$  h<sup>-1</sup> were obtained. The Coupling reactions in which one coupling partner contains a nitrogen donor are typically difficult to accomplish <sup>[31]</sup>. It is therefore noteworthy that the catalyst **CPFO-M** successfully promoted the coupling reactions of 4-bromoaniline with phenylboronic acid and up to 90% yield was obtained (entry 7). Unfortunately, for aryl chlorides, which are much more difficult to activate than aryl iodides and bromides, only low yields were obtained even under prolongation of the reaction time (entries 15–18). Therefore, much more effort is needed to develop new catalysts which are more effective in connection with the Suzuki coupling reactions of unreactive aryl chlorides.

### 3.5. Recyclability of the catalyst

The recycling performance of the catalyst was investigated using the reaction of 4-nitrobromobenzene and phenylboronic acid. As shown in **Fig. 6**, the catalyst could be reused ten times with a slight loss in yield from 98% to 87%. The decrease could be mainly attributed to unavoidable loss of the catalyst during the process of collection. The results confirm that the catalyst has good stability and recyclable applicability for the Suzuki coupling reaction under our experimental conditions.



Fig. 6. The reuse of the catalyst

### 4. Conclusions

Mesoprous Cu-Pd ferrites with high specific surface areas and pore volumes were successfully synthesized by using mesoporous MCM-41 and SBA-15 molecular sieves as templates. The catalysts have shown excellent catalytic performances in the Suzuki coupling reaction, especially the one replicated from MCM-41, and up to  $36.9 \times 10^3$  h<sup>-1</sup> TOF has been obtained. What's more, the catalyst can be magnetically separated easily and exhibited excellent reusability. Expectedly, the catalyst can be applied in large-scale industrial synthesis.

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BET surface area, Fore volume, Fore traineter and Fu content of the samples.					
Catalyst	BET	Pore volume	Pore diameter	Pd content	
	$(m^2 \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$	(nm)	(wt %)	
CPFO-A0	50.3	0.14	13.9	0.21	
CPFO-A1	52.6	0.15	12.9	0.87	
CPFO-A	56.4	0.16	14.2	0.44	
CPFO-S	121.4	0.32	7.7	0.24	
CPFO-M	167.2	0.28	3.6	0.14	

### Table 1

BET surface area, Pore volume, Pore diameter and Pd content of the samples.

**Table 2** The Suzuki reaction of bromobenzene and phenylboronic acid catalyzed by

 different catalysts <sup>a</sup>

	$R_1$ Br+	(HO) <sub>2</sub> B	$R_2$ -	CPFO-M K <sub>2</sub> CO <sub>3</sub> ,EtOH/H <sub>2</sub> O			$R_2$
Enters	Catalyst	D	D	Temperature	Time	Yield <sup>b</sup>	TOF <sup>c</sup> /h <sup>-1</sup>
Entry	Catalyst	$\mathbf{K}_1$	$\mathbf{K}_2$	(°C)	(h)	(%)	(×10 <sup>3</sup> )
1		4-NO <sub>2</sub>	Н	70	0.5		
2	CPFO-A	4-NO <sub>2</sub>	Н	70	0.5	39	3.14
3	<b>CPFO-S</b>	4-NO <sub>2</sub>	Н	70	0.5	81	11.97
4	CPFO-M	4-NO <sub>2</sub>	Н	70	0.5	98	24.83
5 <sup>d</sup>	Pd/CoFe <sub>2</sub> O <sub>4</sub>	4-NO <sub>2</sub>	Н	Reflux	12	92	$0.05^{f}$
6 <sup>e</sup>	Pd/NiFe <sub>2</sub> O <sub>4</sub>	4-NO <sub>2</sub>	Н	90	0.25	95	$3.80^{\mathrm{f}}$
7	CPFO-A0	4-MeO	4-Cl	80	12	35	0.25
8	CPFO-A	4-MeO	4-Cl	80	12	95	0.32
9	CPFO-A1	4-MeO	4-Cl	80	12	97	0.17

<sup>a</sup> Reaction condition: aryl halide (0.5 mmol); boronic acid (0.6 mmol); K<sub>2</sub>CO<sub>3</sub> (1

mmol); solvent (EtOH/H<sub>2</sub>O (v/v=1:1) 1 mL); catalyst 3.0 mg.

<sup>b</sup> Isolated yield by column chromatography.

- <sup>c</sup> TOF (turnover frequency) = mols of coupling product /mols of Pd/time.
- <sup>d</sup> From the reference [14]. Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol of boronic acid, 1.25 mmol of Na<sub>2</sub>CO<sub>3</sub>, 2 mg of Pd–CoFe<sub>2</sub>O<sub>4</sub> (atomic percent of Pd is 1.13%), 5 mL ethanol.
- <sup>e</sup> From the reference [21]. Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), base (2 mmol), 4 mL of 1:1 DMF/H<sub>2</sub>O and Pd/NiFe<sub>2</sub>O<sub>4</sub> (0.1 mol%) at 90 °C.

<sup>f</sup>Based on the data from the references.

<b>Table 3</b> Optimization of the reaction conditions
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	O <sub>2</sub> N-	$Br + \sum B(OH)_2$	Catalyst Base	O <sub>2</sub> N-	<b>&gt;</b>
Enters	Catalyst	Colvert	Dese	$\mathbf{V}_{i}$	TOF <sup>c</sup> /h <sup>-1</sup>
amou	amount (mg)	Solvent	Base	Y leid <sup>*</sup> (%)	(×10 <sup>3</sup> )
1	3	Acetonitrile	K <sub>2</sub> CO <sub>3</sub>	Trace	
2	3	Water	$K_2CO_3$	Trace	
3	3	EtOH	$K_2CO_3$	18	4.56
4	3	EtOH/H <sub>2</sub> O (1:1)	$K_2CO_3$	98	24.83
5	3	EtOH/H <sub>2</sub> O (1:1)	Na <sub>2</sub> CO <sub>3</sub>	28	7.09
6	3	EtOH/H <sub>2</sub> O (1:1)	K <sub>3</sub> PO <sub>4</sub>	93	23.60
7	3	EtOH/H <sub>2</sub> O (1:1)	CsCO <sub>3</sub>	34	8.60
8	3	EtOH/H <sub>2</sub> O (1:1)	NaOH	Trace	
9	3	EtOH/H <sub>2</sub> O (1:1)	None	Trace	
10	2	EtOH/H <sub>2</sub> O (1:1)	$K_2CO_3$	97	36.90
11	4	EtOH/H <sub>2</sub> O (1:1)	$K_2CO_3$	99	18.80

<sup>a</sup> Reaction condition: 4-nitrobromobenzene (0.5 mmol); phenylboronic acid (0.6 mmol); catalyst **CPFO-M**; base (1 mmol); solvent(1 ml); T=70 °C; t= 0.5 h.

- <sup>b</sup> Isolated yield by column chromatography.
- <sup>c</sup> TOF (turnover frequency) = mols of coupling product /mols of Pd/time.

Table 4 Suzuki coupling reaction of various aryl halides and arylboronic acids <sup>a</sup>

,				CPFO-M		
R <sub>1</sub>	×_/	X + (HO) <sub>2</sub> B	$X_{R_2}$	K <sub>2</sub> CO <sub>3</sub> ,EtOH/H <sub>2</sub> O		$\mathcal{A}_{R_2}$
Entry	X	R <sub>1</sub>	<b>R</b> <sub>2</sub>	Time (h)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> /h <sup>-1</sup> (×10 <sup>3</sup> )
1	Ι	Н	Н	0.5	91	34.60
2	Br	Н	Н	2	90	8.55
3	Br	4-NO <sub>2</sub>	Н	0.5	97	36.90
4	Br	4-COOH	Н	6	84	2.66
5	Br	4-Me	Н	5	98	3.72
6	Br	2-Me	Н	5	80	3.04
7	Br	$4-NH_2$	Н	6	90	2.85
8	Br	4-MeO	Н	6	99	3.14
9	Br	4-OH	Н	4	72	3.42
10	Br	4-Me	4-Me	4	99	4.70
11	Br	4-Me	4-Cl	5	94	3.57
12	Br	4-Me	5-NO <sub>2</sub>	5	59	2.24
13	Br	4-MeO	4-Me	5	98	3.72
14	Br	4-MeO	4-Cl	6	88	2.79
15 <sup>d</sup>	Cl	4-CN	4-Me	13	57	0.83
16 <sup>d</sup>	Cl	4-Me	4-Me	13	23	0.34
17 <sup>d</sup>	Cl	Н	4-Me	13	28	0.41
18 <sup>d</sup>	Cl	Н	Н	13	21	0.31

<sup>a</sup> Reaction condition: aryl halide (0.5 mmol); boronic acid (0.6 mmol);  $K_2CO_3$  (1 mmol); solvent (EtOH/H<sub>2</sub>O (v/v=1:1) 1 mL); catalyst (2 mg); T=70 °C.

<sup>b</sup> Isolated yield by column chromatography.

<sup>c</sup> TOF (turnover frequency) = mols converted/mol of active site/time.  ${}^{d}T=90 {}^{\circ}C$