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

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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_2 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 $36.9 \times 10^3\ h^{-1}$ and no obvious decrease in the activity was observed after ten consecutive runs.

1. Introduction

The Suzuki coupling reaction is one of the most important reactions in processes of forming carbon–carbon bonds [1–4], especially for the preparation of biaryls [5–8]. Generally, the Suzuki coupling reactions are catalyzed by homogeneous Pd-containing catalysts [9–11]. 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 [12], Pd catalysts supported by functionalized mesoporous SBA-15 [13], silica [14] and terpolymers [15], etc. Recently, magnetic nanoparticles (MNPs), 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 [16–19]. 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 [19–23]. 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'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 PerkinElmer ICP/6500 atomic emission

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spectrometer. ^{1}H NMR and ^{13}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 [24] as follows: 2.5 g of the nitrate salts in stoichiometric proportion was 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). $Cu_{0.99}Pd_{0.01}Fe_2O_4$ was prepared by using SBA-15 and MCM-41 as templates and designated as CPFO-S and CPFO-M, respectively. For comparison, solid $Cu_{0.995}Pd_{0.005}Fe_2O_4$, $Cu_{0.99}Pd_{0.01}Fe_2O_4$ and $Cu_{0.98}Pd_{0.02}Fe_2O_4$ ferrite nano-powders were synthesized according to the sol–gel auto-combustion route described in our previous work [25] and designated as CPFO-A0, CPFO-A, and 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 $MgSO_4$, 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 ^{1}H NMR and ^{13}C NMR spectra.

3. Results and discussion

3.1. Characterization 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 $CuFe_2O_4$ (JCPDS No. 34-0425) [26,27]. The eleven peaks at 18.3°, 29.8°, 34.6°, 35.9°, 37.1°, 41.6°, 43.8°, 58.0°, 62.0°, 63.8° and 74.7° can be ascribed to the reflection of (1 0 1), (1 1 2), (1 0 3), (2 1 1), (2 0 2), (0 0 4), (2 2 0), (3 2 1), (2 2 4), (4 0 0) and (4 1 3) diffractions of $CuFe_2O_4$. The diffraction peaks in Pd-doped samples were shifted 0.02–0.08° to lower 2θ values as compared to the un-doped samples. This implies that Pd was doped in the lattice of $CuFe_2O_4$ and formed ferrite solid solutions.

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 and b) show highly ordered mesoporous structures, which are in agreement with the literature [28,29]. Fig. 2c and d shows 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.

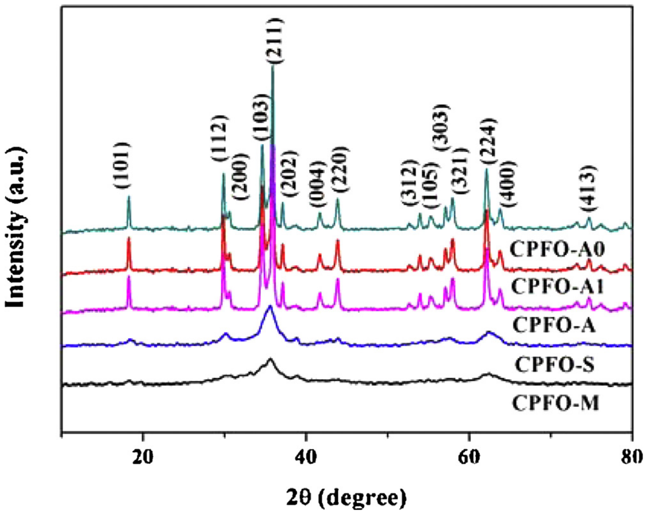

Fig. 1. The XRD patterns of the samples.

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 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_2 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 $m^2 g^{-1}$ 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.

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