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Ultrasonic Synthesis of Pd/SBA-15 Catalyst for Suzuki-Miyaura Coupling

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Abstract. Palladium nanoparticles (Pd NPs) supported on the surface of SBA-15 nanocomposites were synthesized by a one-step, facile ultrasonic method. The Pd/SBA-15 nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption-desorption. The Pd NPs had an average size of 20.9 nm in the 3%Pd/SBA-15. The conversion of 4-bromotoluene catalyzed by 3%Pd/SBA-15 reached 97.49% with 0.1 mmol% catalyst at room temperature without any phase transfer agents, toxic solvents or inert atmosphere. In addition, 3%Pd/SBA-15 nanocomposite could be reused for 3 times with an obvious loss of activity.

Introduction

Palladium (Pd) catalyzed carbon-carbon coupling reactions have been well-known for many years and Pd-based nanomaterials have received considerable attention as catalysts because of its extensive adaptability and improved catalytic activity [1,2].

Heterogeneous Pd catalysts are preferred over homogeneous catalysts due to their facile separation from the reaction mixture and the possibility of recycling [3,4]. The key to prepare the supported Pd nanocomposits is to uniformly disperse Pd NPs on the surface of supports, such as metal oxides [5], carbon materials [4], porous materials [6,7], and polymers [8].

SBA-15 are preferred to be an ideal host for the deposition of Pd NPs, due to its large specific surface area, highly uniform 2D hexagonal array of pores, good thermal and mechanical stability. Many research groups have focused on the synthesis of Pd/SBA-15 nanocomposites. Much of the attempts is chemical reduction of Pd precursors by strong reductants (e.g. $NaBH_4$ and N_2H_4) invovling the use of surfactant molecules or stabilizer to prevent the Pd nanoparticles (NPs) from aggregating [7,9].

The ultrasonic reduction method is a new technology that has shown to be effective for preparing noble metals NPs. However, few studies have been performed on the synthesis and characterization of Pd/SBA-15 nanocomposites by ultrasonic treatment without any stabilizer.

In this work, we present a facile and green synthesis method for fabricating Pd/SBA-15 nanocomposites by ultrasonically treating Pd precursors in ethylene glycol. The as-prepared catalyst exhibited excellent catalytic performance in Suzuki-Miyaura coupling reactions with only 0.1 % catalysts, even in mild conditions. The catalyst can be reused three times without a significant loss of activity.

Preparation of Pd/SBA-15 catalysts

In a typical ultrasonic synthesis of Pd/SBA-15 nanocomposites, 0.5g of SBA-15 in 30 mL of ethylene glycol was mixed using an ultrasonic bath at a frequency of 25 kHz and an input power of 100 W for 30 min. The reaction temperature was maintained at 30 ± 1 ^{o}C by water surrounding the reactor. Next, a required amount of the aqueous Na_2PdCl_4 (0.05 mol/L) solution was rapidly added to the container and mixed under ultrasonic waves with an input power of 400 W for 30min. The final black solid, was centrifuged and washed with deionized water three times, subsequently dried at 70 °C in an oven overnight, and ground into a fine powder. As the amount of Pd, they were denoted here as 1%Pd/SBA-15, 2%Pd/SBA-15, 3%Pd/SBA-15 and 5%Pd/SBA-15 nanocomposites.

General procedure for the Suzuki coupling reactions

In a typical run, a mixture of 4-bromotoluene (2.5 mmol) and K_2CO_3 (691.0 mg, 5.0 mmol) and 30 ml of EtOH/water (1:1) was stirred under a magnetic stirring. Then, the required amount of the Pd/SBA-15 (0.1 mmol%, 0.25 μmol,) were added. Finally, phenylboronic acid (365.8 mg, 3.0 mmol) was added to mixture. The reaction was carried out for 30min in a water bath at 60℃. After completion of the reaction, the mixture was extracted with ethyl acetate three times. The organic layers were combined and evaporated under reduced pressure to obtain crude product which was purified afterwards by column chromatography. The purity of the products was identified by HPLC analysis, and yields were calculated on the basis of aryl halides.

Result and discussion

Fig.1 presents the wide-angle XRD patterns of SBA-15 and Pd/SBA-15 with different amount of Pd. SBA-15 (Fig.1a) shows a broad diffraction peak at 22.5°, which was attributed to the amorphous SiO_2 [6]. Compared with the pure SBA-15, the Pd/SBA-15 nanocomposites started to appear the characteristic peak of Pd. Only a broad modulation of the most intense (111) line of metallic Pd is observed at 2θ= 40.1° for the samples with a Pd load of 1 wt% (Fig. 3b). Up to a Pd amount of 5 wt% (Fig. 3d) shows five weak peaks at 2θ = 40.1°, 46.6°, 68.1°,81.9° and 86.3° are attributed to the (111), (200), (220), (311) and (222) planes of Pd nanoparticles [4], which indicated that the Pd nanoparticles had been successfully loaded onto the channels of SBA-15.

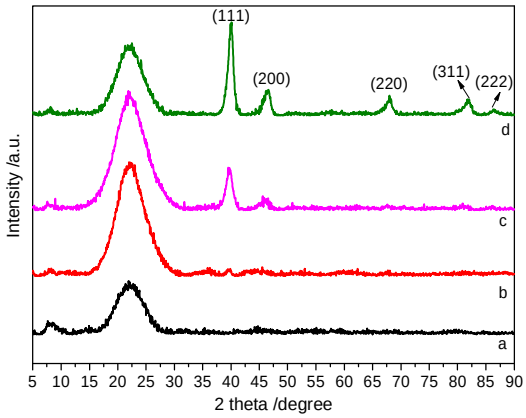

Fig. 1 XRD patterns of (a) SBA-15, (b) 1% Pd/SBA-15, (c) 3% Pd/SBA-15 and (d) 5% Pd/SBA-15

Nitrogen adsorption-desorption experiments were performed on the SBA-15 and Pd/SBA-15 catalysts (Fig. 2). The isotherm of the SBA-15 illustrated typical type IV adsorption isotherms with a H1 hysteresis loop, implying this material had uniform pores and long range cylindrical channelsn [7], which was in good agreement with the results of TEM. The overall form of the N_2 adsorption -desorption isotherms of the Pd/SBA-15 nanocomposites was similar to that of the pure SBA-15 (Fig. 2), suggesting that they retained ordered structure.

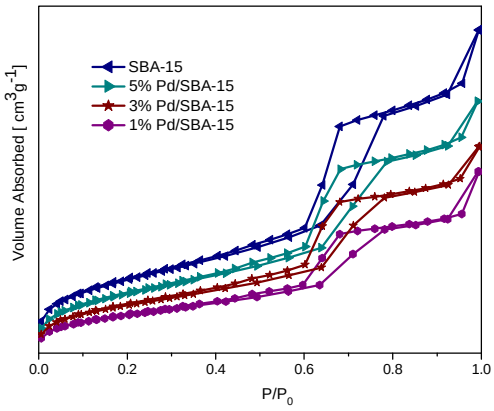

Fig. 2 N_2 adsorption-desorption isotherms of SBA-15 and Pd/SBA-15 with different amount of Pd

As shown in Table 1, the BET surfaces decreases to 496.107 m^2g^{-1} and 347.345 m^2g^{-1} and the pore volume also decreases accordingly in the 1% Pd/SBA-15 and 3% Pd/SBA-15, respectively. The decrease suggests that Pd at least partially located inside the the channels of support. Compared to 3% Pd/SBA-15 nanocomposite, the BET and the pore volume is increased in 5% Pd/SBA-15 nanocomposite. A possible reason for this is that the particles with large particle size are formed and moved from the channel to surface of support. This resulted will be evidenced by TEM.

Table 1 Textural properties of the SBA-15 and Pd/SBA-15

Sample	BET surface area [m^2g^{-1}]	Pore volume [cm^3g^{-1}]	Pore size [nm]
SBA-15	530.737	0.888	6.220
1% Pd/SBA-15	496.107	0.711	5.557
3% Pd/SBA-15	347.345	0.675	5.513
5% Pd/SBA-15	387.011	0.678	5.573

Fig. 3 shows the TEM images of SBA-15 and Pd/SBA-15 nanocomposites. From the images of the SBA-15 (Fig. 3a, b and c), it exhibited the high-ordered hexagonal channel of the mesopore structure. For the 1%Pd/SBA-15 nanocomposite (Fig. 3d), the amount of Pd present was too low to the slightly decrease of BET surfaces and pore volume (Table 1). Fig. 3e clearly demonstrates that in 3%Pd/SBA-15 nanocomposite, Pd NPs were partially located in the mesopore channel of support. As shown in Fig.3f, at a high amount of Pd (5%Pd/SBA-15), the Pd NPs tended to aggregate and migrated to the outside of the channel, which was a detrimental factor that would decrease catalytic activity. The size of 3%Pd/SBA-15 ranges from 13.2 nm-29.1 nm (an average diameter of about 20.8 nm).

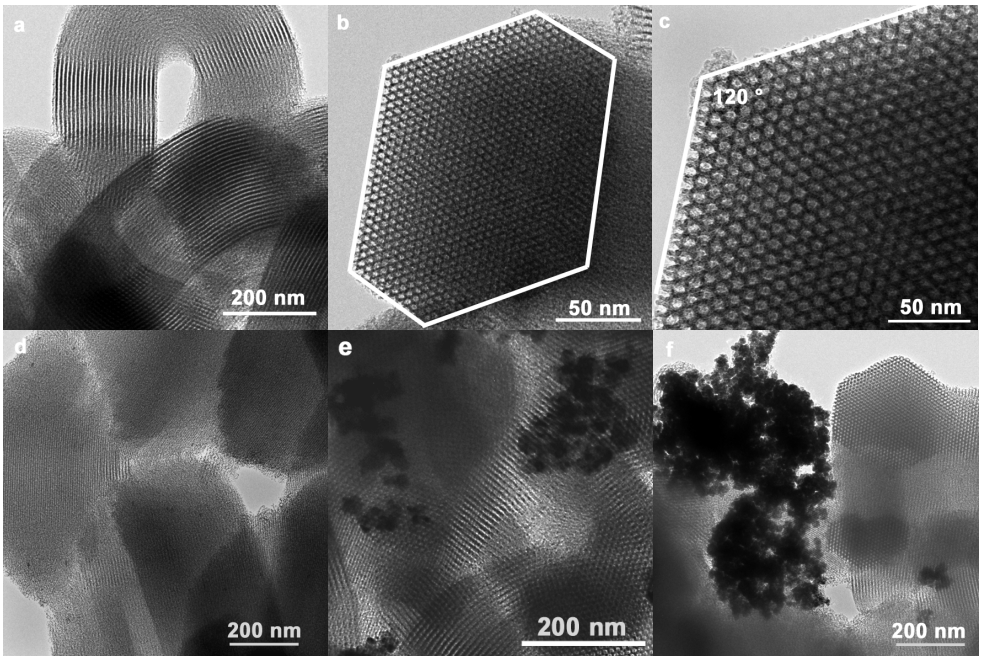

Fig. 3 TEM images of (a) (b) (c) SBA-15, (d) 1%Pd/SBA-15, (e) 3%Pd/SBA-15 and (f) 5%Pd/SBA-15

Fig. 4a shows the yields at different intervals with various catalyst. No conversion of 4-bromotoluene was observed in the presence of only the support SBA-15. Among all the catalysts with different Pd loads, the 3%Pd/SBA-15 exhibited the best and fastest catalytic activity; the conversion of 4-bromotoluene reached to 95.48% at 30 min and, up to 97.89% at 60 min with 0.1 mmol% catalyst. These result indicates high amount of Pd may not only lead to increased production cost, but also to lower catalytic activity resulting from increased particle size and aggregation, as supported by the TEM analysis (Fig. 3). This catalyst could be recycled simply by centrifugation. In addition, the yield decreased to 85.6% (Fig. 4b) in the third cycle, but it decreased to 66.31% (Fig. 4b) in the forth cycle.

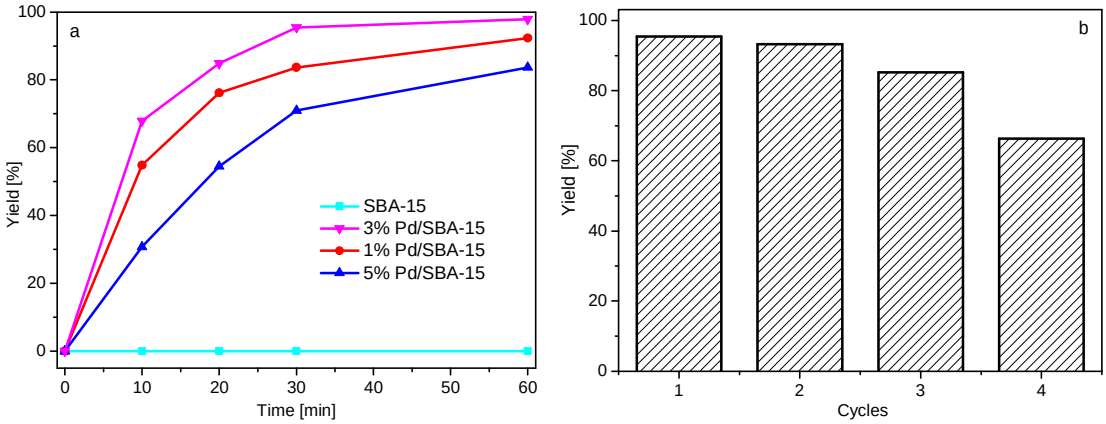

Fig. 4 (a) Yields of biphenyl at different intervals with various catalyst and (b) The reusability of the 3% Pd/SBA-15 catalyst for the Suzuki-Miyaura coupling reaction

Conclusions

In summary, an effective Pd/SBA-15 nanocomposite was designed and successfully prepared by ultrasonically treating an Na_2PdCl_4 precursor solution in ethylene glycol. Pd nanoparticles with an average particle size of 20.9 nm are obtained for 3%Pd/SBA-15. The conversion of 4-bromotoluene catalyzed by 3%Pd/SBA-15 reached 97.89% with 0.1 mmol% catalyst under mild reaction conditions. In addition, the yiled of 3%Pd/SBA-15 nanocomposite was 85.6% after recycling three times.

Acknowledgements

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