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Research paper

Synthesis of a novel ZnO nanoplates supported hydrazone-based palladacycle as an effective and recyclable heterogeneous catalyst for the Mizoroki-Heck cross-coupling reaction

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A new hydrazone-based palladacycle complex was successfully prepared onto ZnO nanoplates support and was fully identified by using a variety of methods such as energy dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller analysis (BET), inductively coupled plasma technique (ICP), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The morphology of nanoplates support has been also confirmed by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). Furthermore, it was shown that ZnO nanoplates supported hydrazone-based palladacycle can act as a highly efficient heterogeneous catalyst for the Mizoroki-Heck cross-coupling reaction with excellent yields. The reaction was successfully carried out between aryl iodides, bromides or even aryl chlorides with a variety of olefins. Additionally, it is possible to isolate the catalyst from the reaction mixture and reused for eight sequential cycles without remarkable decrease in catalytic activity.

1. Introduction

Palladium-catalyzed processes facilitate the formation of C—C bonds between aryl halides and vinyl groups via Mizoroki-Heck type reactions, which provide a versatile, effective and common way for the synthesis of various substituted olefins [1–3]. Therefore, palladium-catalyzed reactions accelerate the organic synthetic routes into a large number of biological and medicinal compounds [4–6]. However, in most of the reactions catalyzed by palladium complexes, in addition to low catalytic efficiency, a catalyst with high loading amount of Pd and an inert atmosphere are commonly required to promote the conversion, which is costly and not suitable from an environmental viewpoint [7]. Thus, utilization of the new palladium complexes as catalyst has been of considerable interest especially regarding aryl chlorides [8–10] under aerobic and aqueous conditions [11–14]. In the past few years, various Pd(II) complexes, such as *N*-heterocyclic carbene [15] and phospha-containing complexes [16] have been applied as catalyst in C—C cross-coupling reactions. In addition, YCY-type [17] and CY-type palladacycles [18,19], in which Y could be various functional groups bound to palladium through P, N, S or O atoms, have also demonstrated their catalytic activities [20,21].

However, palladacycles are known to be the most efficient catalysts among the other Pd(II) complexes [22,23]; and between the several types of palladacycle catalysts, CN-type palladacycles, which exist typically as bridged dimers by halogen or acetate, are one of the most effective palladium catalysts for carbon-carbon bond formation due to having a highly energetic C—Pd bond [24,25], in which the nitrogen atom can be from amine [26,27], imine [28,29], oxime [30], hydrazone [31] or *N*-heterocycle ligands and etc. Also, the metalated carbon is usually an aromatic sp^2 carbon. For example, Iyer reported the cyclopalladated acetylferrocenyl oxime as a CN-type palladacycle in the Mizoroki-Heck coupling reaction [32]. Nowtony [33] and Wu [34] also investigated the use of imino-palladacycle complexes in this type of C—C coupling reaction in good yields.

Although, the palladacycle catalysts as Herrmann described, are effectively able to promote many reactions, similar to Heck coupling reaction [35], these catalysts suffer from some disadvantages associated with their instability, the necessity of using toxic phosphine auxiliary ligands, degradation, deactivation of catalyst during the first run as well as palladium leaching and difficult separation [36]. However, to the extent of our knowledge, a little research on the stability, recovery and reusability of these catalysts has been performed in the literature. In recent years, efforts have been made to solve the problem by immobilization of palladacycles on different supports. Accordingly, Nowotny et al. immobilized

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the previously synthesized imine-based palladacycle complex onto polystyrene to improve its reusability for the Heck reaction. However, it failed after the second run [33]. As a result, a phospha-containing ligand was used for the recovery of the Pd catalysts during the reaction [37–42]. Afterwards, Gladysz prepared an imine-type palladacycle immobilized onto a thermomorphic fluorous polymer, in which recyclability of the catalyst was enhanced significantly; but this reactivity was not observed for aryl bromides [43]. Moreover, Alonso et al. used the graphene oxide supported oxime-palladacycle in the coupling reaction, in which the efficiency of the catalyst was missed in third run [44]. In this manner, some palladacycles were immobilized onto polystyrene [45–48], chitosan [49], polyethylene glycol [50], Fe_3O_4 nanoparticles [51], MCM-41, SiO_2, polystyrene-divinyl benzene polymer [52] and polyvinyl pyridine [53] supports to obtain an improved heterogeneous catalyst. But these catalysts have still been suffering from the problem of low reusability and low catalytic activity, especially for aryl bromides and chlorides. Therefore, the exploration of new stable palladacycles is still required. To the best of our knowledge, no research dealing with immobilization of a palladacycle onto ZnO support has been reported. ZnO is a valuable material in biomedicine, ceramics, ointments, foods, etc. [54] due to its exceptional physical and chemical properties including high chemical, thermal and mechanical stability [55], hardness, biocompatibility and biodegradability, antibacterial and non-toxicity [56–58]. Furthermore, ZnO nanoparticles, by having high surface area to volume ratio and considerable stability as mentioned above, are expected to be an efficient, suitable, and stable heterogeneous support for organic catalytic centres [59–62]. Therefore, in continuation of our research interest in preparing of heterogeneous nano catalysts [63–66], we are intending to prepare a new hydrazone-based palladacycle which can be immobilized onto ZnO nano support to promote its stability and catalytic activity. To do so, we chose a hydrazone ligand containing carboxylate groups; because carboxylate onions strongly adsorbs Zn centres and significantly adjusts the surface morphologies by promoting or reducing the crystal growth as well [67–70]. Although, organic additives have been widely used to alter the crystal growth of ZnO nanoparticles, but this strategy has not been used for immobilization of organometallic catalytic centres onto ZnO nanostructure support.

Herein, for the first time, we report the synthesis of a novel ZnO nanoplates supported hydrazone-based palladacycle which can be applied as a highly effective and reusable palladacycle catalyst for running Mizoroki-Heck cross-coupling reaction between aryl halides and various olefins with high yields in short reaction times even for aryl chlorides.

2. Experimental

2.1. Materials and instruments

All chemical materials were supplied from Aldrich, Merck and Fluka. A Buchi or Heidolph rotary evaporator was employed to remove solvents at reduced pressure. Thin layer chromatography plate was prepared on plates of silica gel 60 (5–40 μm mesh size diameter) on glass plates ($20 \times 20\ cm^2$) using 10 g of silica gel. IR spectroscopy was accomplished by a Shimadzu FTIR-8300 spectrophotometer. ^1H and ^{13}C NMR of the resulting Mizoroki-Heck products were provided with Bruker Avance spectrometer at 300 and 75 MHz, respectively. Inductively coupled plasma technique was performed by Varian Vista-MPX instrument to determine the amount of metal. Thermogravimetric curve was recorded under nitrogen atmosphere by NETZSCH STA 409 PC instrument. Energy dispersive X-ray analysis was achieved using Vega TESCAN-Model scanning electron microscope supplied with energy dispersive X-ray equipment. X-ray diffraction was performed using a PHILIPS X-ray diffractometer system (PW1800-Model). The surface morphology of the ZnO nanoplates supported hydrazone-based palladacycle catalyst was analysed by scanning electron microscope (KYKY-EM3200 Digital Scanning). A 2400 series II PerkinElmer elemental analyzer was employed for the CHN analysis. A twin anode X-ray source system (XR3E2, 8025-BesTec) was applied for X-ray photoelectron spectroscopy analysis. The specific surface area of the nanostructure was determined by the nitrogen sorption measurement, ([5.0.0.3] Belsorp, BEL Japan, INC.). The porous structural parameter in this paper is based on Barret-Joyner-Halenda (BJH) data. The NMR spectra of the products in Table 5 were provided with electronic Supplementary information (ESI).

2.2. Synthesis of the catalyst

2.2.1. Synthesis of hydrazone ligand (1)

4-formylbenzoic acid (0.300 g, 2 mmol) was dissolved in dry MeOH (20 mL) at room temperature and then hydrazine hydrate·$6H_2O$ (0.1 mL, excess) was added dropwise to the solution according to the literature procedure with slightly modification [71]. After a few minutes yellow crystals precipitated. The product was collected by filtration, washed with MeOH and acetonitrile, and then dried under vacuum condition. As a result, the compound (1E,2E)-1,2-bis(1,4-hydraziniumbenzoyl)ethylidene) hydrazine was synthesized as yellow fine powder (0.3 g, 95%). δH (300 MHz; [D6] DMSO; Me_4Si): 7.07 (10H, br s, NH_2-NH_3^+), 7.57 (^3J = 8.9, 4H, d, CH), 7.82 (^3J = 8.9, 4H, d, CH), 8.66 (2H, s, CH = N); δC (75 MHz; [D6] DMSO; Me_4Si): 129.9 (CH), 130.0 (CH), 139.0 (C), 140.0 (C), 162.4 (C = N), 172.4 (COO^-). Also, elemental analysis was performed to confirm the synthesis of the ligand (Found: C, 53.3; H, 5.1; N 22.7. Calc. for $C_{16}H_{20}N_6O_4$: C, 53.3; H, 5.5; N, 23.3%).

2.2.2. Synthesis of ZnO nanoplates supported hydrazone ligand (hydrazone@ZnO, 2)

ZnO nanoplates supported hydrazone ligand was synthesized by reacting $Zn(NO_3)_2{\cdot}6H_2O$ (1.18 g, 4 mmol) with the prepared hydrazone ligand (**1**) (0.3 g) in 25 mL DMF in a sealed vessel reaction. Then the yellow solution was heated at 90 °C for 18 h. As soon as the solution temperature reached to 90 °C, ZnO nanoplates hydrazone ligand rapidly was produced from solution. After 18 h, the resulting pale yellow powder was collected by filtration, washed with DMF and subsequently with chloroform and dried under vacuum for 2 h to give ZnO nanoplates supported hydrazone ligand (**2**).

2.2.3. Synthesis of ZnO nanoplates supported hydrazone-based palladacycle catalyst (hydrazon-Pd@ZnO, 3)

To 0.3 g ZnO nanoplates supported hydrazone ligand was added 0.045 g $Pd(OAc)_2$ and 100 mL dry dichloromethane as solvent. The lemon mixture was stirred at room temperature for 1 day. Subsequently, the cream-green mixture was centrifuged and washed several times with dichloromethane and allowed to dry at 80 °C.

2.3. General procedure for Mizoroki-Heck coupling reaction of aryl halides with olefins

To a 25 mL round bottom flask containing aryl halide (1 mmol), olefin (1.2 mmol), Et_3N (1.5 mmol), and ZnO nanoplates supported hydrazone-based palladacycle (10 mg, 0.26 mol% Pd), 3 mL DMF was added as solvent. The resulting solution was stirred at 130 °C in an oil bath. The reaction was followed by TLC (thin layer chromatography) and at the end; it was allowed to cool to room temperature and was centrifuged to separate the catalyst. The residue was diluted with ethyl acetate (2×5 mL), and washed with water (2×5 mL). Then the organic phase was dried with