Catalysis Communications 113 (2018) 27–31

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Ag_1Pd_1-rGO nanocomposite as recyclable catalyst for CDC reactions of 2-arylpyridines with aldehydes

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ARTICLE INFO

Keywords:
Heterogeneous catalysis
Ag_1Pd_1 alloy nanoparticle
Reduced graphene oxide
Recyclable catalyst
C − H acylation

ABSTRACT

Ag_1Pd_1 nanoparticle-reduced graphene oxide (Ag_1Pd_1-rGO) nanocomposite was used as an efficient catalyst for the synthesis of aromatic ketones via cross dehydrogenative coupling (CDC) reactions of 2-arylpyridines with aldehydes. The catalyst can be reused for 5 cycles without significantly losing its catalytic activity. On the basis of the obtained experimental evidence, we proposed a possible mechanism for the heterogeneous catalysis. We find that the supported catalysts exhibit a set of benefits, including extraordinarily catalytic activity, high reusability and remarkable tolerance of a variety of substrates.

1. Introduction

A major theme in organic synthetic community is to develop ecologically and economically advantageous reactions which have the ability to transform simple precursors to multifunctional compounds or natural products [1]. Due to the abundance of C—H bonds in the starting substrates, direct and efficient conversion of these C—H bonds to C—C bonds is of significant importance [2–5]. Indeed, the past decade has witnessed the rapid development in C—H activation capable of leading to arene-arene or arene-alkane linkages [6]. The reported C—H activation strategies oftentimes relies on directing-group assisted C—H bond functionalization [7] or dehydrogenative cross-coupling [8,9]. In both strategies, catalyst, functionalized partner, and oxidant should be screened carefully to proceed the C—H bond cleavage and subsequent C—C bond formation effectively [10,11].

Aromatic ketones are an important class of chemicals which have widespread applications in the synthesis of pharmaceuticals, fragrance, dye and agrochemical industries [12]. The classical synthesis of aryl ketones is based on the use of Friedel-Crafts acylation of aromatics in the presence of solid acids, such as acid-treated metal oxides and heteropoly acids [13]. In comparison, the direct introduction of carbonyl functionality into aromatic motifs via C—H bond cleavage is more eco-friendly alternative. In fact, the synthesis of such compounds has achieved considerable advances via directed C—H bond activation [14]. A typical strategy is by use of direct acylation of 2-phenyl pyridines with a variety of potential acyl sources, such as aldehydes [15], alcohols [16], toluenes [17], α-oxocarboxylic acids [18], α-diketones [19], benzylamines [20] and alkenes/alkynes [21,22]. The reactions are commonly carried out in the presence of transition metal salts as homogenous catalysts, including $Pd(OAc)_2$ [15,17,19,22], $PdCl_2$ [16,20,21], $Pd(PhCN)_2Cl_2$ [18]. While the use of such homogeneous catalysts usually offers high selectivity and efficiency, the unrecyclable nature of the metal salts tremendously increases the economic cost in the practical use [23]. In addition, utilization of homogeneous catalysts definitely complicates the step of product purification and sometimes can lead to environmental concerns, especially for the case of needing for toxic phosphine compounds as ligands [24].

The use of Pd nanoparticles for C—H bond activation is expected to provide an alternative pathway to address the aforementioned issues [25]. In addition to catalyzing C—C coupling [26,27] and alkene hydrogenation [28], Pd nanoparticles have proven to possess comparable catalytic activity to palladium salts in C—H bond functionization. For example, the use of $Pd/\gamma\text{-}Al_2O_3$ (3 wt%) as catalyst led to the reaction of 2-phenylpyridine with benzaldehyde with a yield up to 88% in the presence of *tert*-butyl peroxybenzoate as oxidant [29]. However, this reaction applied unsuccessfully to aliphatic aldehydes, and the recyclability of the catalyst was not good. We reason that the catalytic performance of Pd nanoparticles in the C—H bond activation allows to be further improved by doping another component in the Pd lattice to form alloy nanoparticles in which a synergistic effect between the constituting elements appears [30]. By making use of Ag_1Pd_1 alloy nanoparticles on reduced graphene oxide (rGO) as catalysts, here we

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https://doi.org/10.1016/j.catcom.2018.05.007
Received 22 January 2018; Received in revised form 10 May 2018; Accepted 14 May 2018

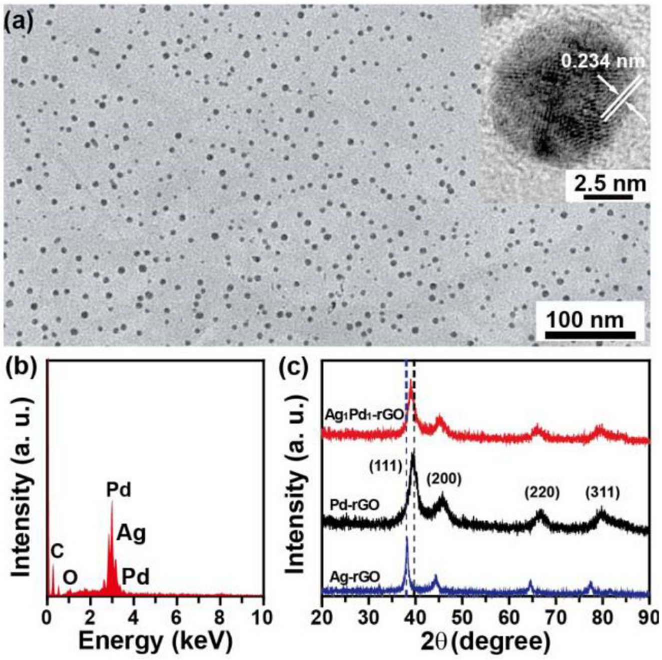

Fig. 1. (a and b) TEM and EDS profile of as-prepared Ag_1Pd_1-rGO nanocomposites, inset in a showing HRTEM image of an Ag_1Pd_1 nanoparticle on rGO. (c) XRD comparison of as-prepared Ag_1Pd_1-rGO, Pd-rGO and Ag-rGO nanocomposites.

report a cooperative effect between the elements of Ag and Pd in cross dehydrogenative coupling reactions of 2-arylpyridines with aldehydes. We find a negligible loss in the catalytic activity of the supported catalyst after 5 successive catalytic cycles. We demonstrate that the heterogeneous catalysts not only have extraordinarily catalytic activity, high reusability, but also remarkable tolerance of a variety of substrates. By combining our experimental evidence with previous findings, we propose a possible mechanism accounting for the heterogeneous catalysis process.

2. Results and discussion

2.1. Characterization of the catalysts

We first synthesized Ag_xPd_y-rGO (x/y = 1/1, 1/3 and 3/1) as well as Ag-rGO (or Pd-rGO) via our reported method (see supporting materials, Fig. S1) [31]. Transmission electron microscopy (TEM) showed that the surface of rGO was homogeneously decorated with Ag_1Pd_1 nanoparticles with an average diameter of 6 nm (Fig. 1a). The high-resolution TEM (HRTEM) image (inset in Fig. 1a) reveals high crystallinity of the loaded nanoparticles, and the *d*-spacing of the lattice fringes (0.234 nm) is in accordance with the lattice parameter of the AgPd alloy [32]. Energy dispersive X-ray spectroscopy (EDS, Fig. 1b) suggested that the atomic ratio of Ag-to-Pd in the alloy nanoparticles is about 1.24/1 that closely matches to the value obtained by inductively coupled plasma optical emission spectrometry (ICP-OES, $m_{Ag}/m_{Pd} = 17.7\%/13.9\%$, $n_{Ag}/n_{Pd} = 1.26/1$). X-ray power diffraction measurement (Fig. 1c) confirmed that the nanoparticles are alloy instead of a mixture of isolated Ag and Pd segments due to the presence of obvious peak shift in the diffraction patterns [33]. Meanwhile, the strong diffraction profiles implied the high crystalline nature of the as-prepared alloy nanoparticles. The character of Ag (0) and Pd (0) in the nanoparticles was further evidenced by X-ray photoelectron spectroscopy (XPS, Fig. S2c). The binding energies for Ag $3d_{3/2}$ (373.6 eV), $3d_{5/2}$ (367.6 eV) and Pd $3d_{3/2}$ (340.2 eV), $3d_{5/2}$ (334.9 eV) are in good agreement with those 3d binding energies for bulk pure Ag and Pd metals, respectively [34]. Other alloy nanoparticles and pure metal nanoparticles were characterized by a similar way before catalytic studies.

2.2. Optimization of the reaction conditions

We carried out catalyst screening for sp^2 C—H bond acylation of 2-phenylpyridine (**1a**) and benzaldehyde (**2a**) in the presence of *tert*-butyl hydroperoxide (TBHP) as an oxidant. We found the use of $Pd(OAc)_2$ (10 mol%) and $Pd(PPh_3)_4$ (3 mol%) offered a yield of 39% and 47%, respectively, after keeping the reaction at 110 °C for 18 h (Table 1, entries 1 and 2). A control experiment showed that indeed no reaction took place in the absence of catalyst (Table 1, entry 3). When replacing $Pd(OAc)_2$ and $Pd(PPh_3)_4$ with heteroneous catalysts of Pd-rGO, a comparable yield was obtained (Table 1, entry 4). To our delight, the yield was substantially elevated to 87% when Ag_1Pd_1-rGO (10 mg, 2.6 mol% Pd) was employed as a heterogeneous catalyst (Table 1, entry 5). The inability of Ag-rGO toward the C—H bond activation (Table 1, entry 6), together with the low catalytic activity of the Pd-rGO, implied a synergistic effect between the Ag and Pd atoms in the acylation of 2-phenylpyridine. The inferior catalytic performance of Ag_1Pd_3-rGO and Ag_3Pd_1-rGO in the model reaction suggested that the synergistic effect is highly dependent on the composition of the alloy nanoparticles (Table 1, entries 7 and 8). On a separate note, the application of commercialized Pd/C as catalyst led to a yield of 5% (Table 1, entry 22), indicating that ordinary Pd^0 heterocatalysts are likely to be ineffective for the cross-dehydrogenative coupling reactions.

Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), catalyst Ag_1Pd_1-rGO (10 mg), and TBHP (0.75 mmol), 110 °C, 18 h under an air atmosphere. Yields of isolated product are listed.

Besides the nature of the catalyst, other reaction parameters, including the amount of catalyst, solvent, oxidant, temperature and atmosphere, also exert a profound impact on the yield. The reaction conditions were optimized as follows: 10 mg of catalyst Ag_1Pd_1-rGO (2.6 mol% Pd), toluene as solvent, TBHP as oxidant, 110 °C under air atmosphere (Table 1, entries 9–21).

2.3. Synthesis of aromatic ketones

Under the optimized reaction conditions, the scope of the acylation reaction of substituted 2-arylpyridines and various benzaldehyde derives was examined (Scheme 1). A variety of benzaldehydes with electron-withdrawing and electron-donating groups, including methyl, methoxy, chlorine and trifluoromethyl, are suitable for this reaction, and the corresponding products (**3a**(**a–h**)) were obtained in good to moderate yields. In general, the reactivity of the electron-withdrawing group-substituted benzaldehydes is higher than that of the electron-withdrawing precursors. This may attribute to the difference in the activity of the substituted benzoyl radicals in situ formed in the reactions. Notably, the yields of 4-, 3-, 2-methoxy-substituted benzaldehydes were decreased in turn, which should be a result of a gradual increase in the steric effect. In addition, various arylpyridines bearing substituents on the benzene rings were also examined, and the results suggested that the functional groups, including electron-donating and -withdrawing ones, were tolerated (**3**(**b–h**)**a**). The CDC reaction was also applicable to other substrates, such as 7,8-benzoquinoline and 1-phenyl-pyrazole (scheme 1, **3ia**, **3ic**, **3if**, **3ja** and **3jc**), to afford corresponding compounds in good yields. To our delight, good yields were obtained as aliphatic aldehydes were used in the Ag_1Pd_1-rGO catalyzed C—H bond acylation reaction (scheme 1, **3ak**, **3al**, **3bl** and **3il**).

It is worth noting that scale-up reaction (15 times) of 2-phenylpyridine (**1a**) with benzaldehyde (**2a**) afforded a yield of 79%, showing the potential utility of the as-prepared catalyst in practical chemical industry.

We also investigated the possibility of using benzyl alcohol and toluene as potential acylation agent under the same conditions (TBHP: