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Interconnected ruthenium dioxide nanoparticles anchored on graphite oxide: Highly efficient candidate for solvent-free oxidative synthesis of imines

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ABSTRACT

Interconnected ruthenium dioxide nanoparticles (RuO₂NPs) anchored graphite oxide nanocatalyst (RuO₂/GO) with good BET surface-area (285 m²/g) was prepared. Under feasible reaction conditions, the RuO₂/GO worked well for oxidative synthesis of imines. The RuO₂/GO catalyzed a broad range of amines including less reactive aliphatic amines in good yields (98–58%) with excellent selectivity (100%). This is the most efficient RuO₂-based nanocatalyst for the synthesis of imines among those reported to date. An indirect two-step method was adopted for the coupling of alcohols and amines, and the results found to be excellent. The reusability, stability and heterogeneity of RuO₂/GO were also investigated.

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Introduction

Imines are very important moieties because of their diverse reactivity, which has directed to essential applications in industrial and laboratory synthetic processes [1]. The imines are highly essential as reactive intermediates and nitrogen sources for the synthesis of fine chemicals, biologically active compounds and their intermediates [2,3]. As an electrophilic reagents, the reactive C=N group of imines has played key role in addition, condensation and cycloaddition reactions [4]. Traditionally, imines were synthesized by the condensation of amines with carbonyl compounds. However, the drawback of these methods is utilization of dehydrating agents as well as Lewis acid catalysts [5]. Recently, the imines are being prepared from the oxidative coupling of alcohols with amines in the presence of metal catalyst under inert (nitrogen or argon) or O₂ atmosphere [6]. Self-condensation of amines is also one of the prime routes to obtain imines [4]. Thus far, several transition-metal based catalysts

including nano-Cu(0) [7], CuO/Fe₃O₄ [8], CuO/CeO₂ [9], Fe-MOF [10], Al/MOF [11], V₂O₅ [12], CeO₂/MoO₃ [13], F-doped CeO₂ [14], MnO_x/HAP [15], meso-Cs/MnO_x [16], Pd/AlO(OH) [17], Pd/ZrO₂ [18], Au/Al₂O₃ [19], Au/TiO₂ [20], Au/CeO₂ [21], Au/C [22], Pt-Fe₂O₃ [23], Ag/Al₂O₃ [24], Ir/CeO₂ [25], and Pt-Sn/γ-Al₂O₃ [26], have been reported. Metal-free carbon based catalysts (graphene oxide, activated carbon and CNTs etc.) are also reported [27]. However, these systems [either metal-free or (un)supported metal-based catalytic systems] are obviously suffered from at least one of the four main points; (1) O₂ atmosphere, (2) higher amount of catalyst, (3) longer reaction time, and (4) reusability. Notably, under solvent-free reaction conditions, most of the catalytic systems showed poor reusability due to unavoidable blocking of catalytic active sites by the reactants and products.

Wide chemical states (–II to +VIII) and tunable properties, ruthenium was found to be a superior catalyst for organic reactions [28,29]. Notably, the RuO₂ is known to be an excellent oxidation catalyst because of its redox properties [30]. However, Ru-based catalysts are found to be inefficient for the imines synthesis [4]. Several Ru-complexes were employed as homogeneous catalysts for imines synthesis, but the reactions are carried out under inert atmospheres or harsh reaction conditions. Whereas, supported Ru catalysts often promoted nitrile formation from benzylamines

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[31]. In 2009, Kim et al. [32], demonstrated that Ru(OH)_x/TiO₂ catalytic system is efficient for the cross-coupling of primary benzylic or cinnamyl alcohols with anilines or aliphatic amines. Later, Cano et al. [33], reported that Ru(OH)₃/Fe₃O₄ can be used for imines synthesis under inert atmosphere, and they found that addition of base (KOH or NaOH) would switch the final products easily. Unfortunately, most of the Ru-based heterogeneous catalysts including Ru/HAP, and RuCl_x/TiO₂ were failed to promote the coupling of amines [34]. Hence, developing an efficient Ru-based heterogeneous catalytic system for the imines synthesis is a challenging task.

Surface area, nature of support, metal-support interaction, structure of catalyst, and particle size are the key factors for the activity of supported metal catalysts [35–38]. Obviously, graphene is a unique 2D material for metal nanoparticles (NPs) due to its important physicochemical properties such as unique structure, high specific surface area, and chemical inertness [39–43]. Efficient nanocatalysts such as CuO/GNS [44], Ru/GNS [45] and RuO₂NRs/GNS [46] were recently reported by our group (where GNS is graphene nanosheets). The results declared that the nanocatalysts are efficient for various organic transformations. Herein, we prepared interconnected ruthenium dioxide nanoparticles (RuO₂NPs) anchored graphite oxide nanocatalyst (RuO₂/GO). The RuO₂/GO was characterized in detail by means of TEM, XPS, XRD, Raman, SEM-EDS, BET and ICP-MS analyses. The RuO₂/GO was employed as a heterogeneous nanocatalyst for the oxidative synthesis of imines.

Experimental

General

Graphite oxide (GO) with >90% purity was purchased from ACS materials, USA. Ru(acac)₃ (97%) and methanol were obtained from Sigma Aldrich. All other chemicals were purchased from Sigma Aldrich or Wako Pure Chemicals. Details of materials characterization and catalytic product conformation are provided in the Supporting information.

Preparation of RuO₂/GO

0.398 g of Ru(acac)₃ and 1.0 g of GO were dispersed in methanol and sonicated for several hours. Subsequently, the mixture was stirred at 65 °C for several hours to evaporate the methanol. The resultant powder was grinded well with mortar and pestle until the homogeneous mixture was obtained and then the resultant mixture was kept under vacuum for 24 h. Finally, the solid mixture was calcinated in the muffle furnace under N₂ atmosphere at 600 °C (heating rate of 5 °C/min) for 3 h. For comparison, pure GO and Ru(acac)₃ were calcinated in the muffle furnace under same conditions (N₂ atmosphere at 600 °C for 3 h) and the resultant powders (RGO and RuO₂) were tested.

Procedure for the self coupling of primary amines

25 mg of RuO₂/GO (0.98 mol% Ru) and 2 mmol of benzylamine were introduced into 25 mL round bottom flask with a magnetic bar. The mixture was stirred under air atmosphere at 100 °C for 3 h. The reaction was monitored by GC analysis. After completion of the reaction, the catalyst was separated by centrifugation and the crude mixture was checked by GC analysis to calculate the conversion, yield and selectivity. The product was further confirmed by NMR and MS(GC) analyses. The catalyst was also separated out from the reaction mixture by simple centrifugation, washed well with diethyl ether, dried at 60 °C, and then reused. (*E*)-*N*-Benzylidene-1-phenylmethanamine (**2a**): ¹H NMR (400 MHz,

DMSO-d₆): δ (ppm) 4.87 (2H, s, PhCH₂), 7.25–7.35 (5H, m, PhH), 7.52 (3H, m, PhH), 7.84 (2H, m, PhH), 8.65 (1H, s, CH=N); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 64.37 (CH₂), 127.14 (CH), 128.26 (CH), 128.35 (CH), 128.72 (CH), 129.03 (CH), 131.10 (CH), 136.44 (C), 139.99 (C), 162.10 (CH); GC-MS (m/z): 195.4.

Procedure for cross-coupling of anilines with primary amines

A mixture of benzylamine (2 mmol), aniline (6 mmol) and catalyst (25 mg, 0.98 Ru mol%) were stirred under air atmosphere at 100 °C for 3 h. (*E*)-*N*-Benzylideneaniline (**5a**): ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 7.08 (1H, m, PhH), 7.45–7.55 (7H, m, PhH), 7.84 (2H, m, PhH), 8.69 (1H, s, CH=N); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 122.3 (CH), 122.4 (CH), 127.3 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 129.2 (CH), 130.1 (CH), 130.1 (CH), 131.1 (CH), 136.5 (C), 152.1 (C), 160.2 (CH); GC-MS (m/z): 180.5.

Procedure for synthesis of imines from alcohols and amines

25 mg of RuO₂/GO (0.98 mol% Ru) and 2 mmol of benzyl alcohol were magnetically stirred under open air atmosphere at 110 °C for 29 h. Subsequently, 2 mmol of benzyl amine was added to the above reaction mixture and stirred for 10 min. (*E*)-*N*-Benzylidene-1-phenylmethanamine (**2a**): ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 4.87 (2H, s, PhCH₂), 7.25–7.35 (5H, m, PhH), 7.52 (3H, m, PhH), 7.84 (2H, m, PhH), 8.65 (1H, s, CH=N); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 64.37 (CH₂), 127.14 (CH), 128.26 (CH), 128.35 (CH), 128.72 (CH), 129.03 (CH), 131.10 (CH), 136.44 (C), 139.99 (C), 162.10 (CH); GC-MS (m/z): 195.4.

Results and discussion

Physicochemical characterization of RuO₂/GO

HRTEM images were taken for GO and RuO₂/GO; the results are provided in Fig. 1. The pure GO is pure, continuous, wrinkled and transparent sheet with an average thickness of about 0.8–2 nm. The fine dispersion of RuO₂ nanoparticles on the surface of GO was explained by referring the HRTEM images (Fig. 1(b–d)). Moreover, the RuO₂ nanoparticles were interconnected to each other and uniformly covered the surface of GO. This interesting morphology might have caused from the uniform aggregation of the RuO₂ nanoparticles during the calcination process. The size of RuO₂ nanoparticles was difficult to measure since the RuO₂ particles are interconnected and irregular in shape. To find out the reason for the formation of this interconnected network-like morphology, carbon nanotubes (CNTs) were also employed as a support. However, the morphology could be seen only with GO. Hence, we concluded that the morphology is highly dependent on the nature of support and, in the present case it is mainly due to the 2D nature of the GO. In addition, the presence of oxygen functional groups on GO might have also contributed for the controlled aggregation of RuO₂ species. No free RuO₂ nanoparticles were found in the background of the HRTEM images (Fig. 1(b–d)), which indicate strong attachment of RuO₂ nanoparticles on GO. To the best of our knowledge, this is the first observation of interconnected ruthenium nanoparticles network reported so far.

Fig. 2 presents the SEM-EDS and their corresponding elemental mapping images of RuO₂/GO. The wt% of Ru, O and C in RuO₂/GO was found to be 4.0, 18.8 and 77.2 respectively (Fig. 2(d)). Similarly, the atom% of 84.1, 15.4, and 0.5 was determined for C, O and Ru respectively. The Ru elemental mapping (Fig. 2(d)) revealed that the distribution of Ru in RuO₂/GO was homogenous. Worth to mention that the RuO₂/GO has a very high BET surface area of 285 m²/g with a pore volume of 0.58 cm³ g⁻¹ and a BJH desorption average pore diameter of 8.1 nm. Generally, most of the

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