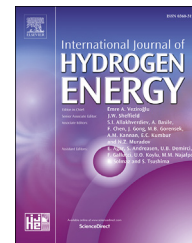




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Polymer-graphene hybride decorated Pt nanoparticles as highly efficient and reusable catalyst for the dehydrogenation of dimethylamine–borane at room temperature

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ABSTRACT

Addressed herein, we report a reduced graphene oxide (rGO) nanosheet coupled with polyaniline (PANI) for platinum (Pt) nanoparticles as supporting materials. The PANI-coupled rGO (PANI@rGO) nanosheet is prepared by a simple one-step chemical assembly strategy, and Pt nanoparticles are anchored on the support of PANI@rGO through the reaction of PANI with a platinum salt. The designed PANI efficiently exposes the surface of rGO sheets and stabilizes metal nanoparticles. Consequently, the Pt@PANI-rGO catalyst exhibits good reusability, durability and high catalytic performance for dimethylamine–borane dehydrogenation reaction. The structure morphology and properties of Pt@PANI-rGO NPs were characterized by using several different techniques such as UV–Vis, XPS, TEM, XRD and HR-TEM-EDX analyses. This newly prepared catalyst can be reused again at low concentrations and temperature. They showed a high turnover frequency (42.94 h^{-1}) and low E_a value of $15.1 \pm 2 \text{ kJ/mol}$ for DMAB dehydrocoupling in the ambient conditions. The proposed nano architecture offers a new pathway to promote the performances of rGO in various applications; moreover, this work provides a powerful and universal synthetic strategy for such an architecture.

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Introduction

Hydrogen-based energy carriers has been considered as a one of the most efficient and the safest methods of hydrogen storage. However, the storage of hydrogen is still a main hurdle for the hydrogen economy. Many hydrogen sources

have been investigated, from the recent studies, ammonia boranes (ABs which is parents of amine boranes) can be considered as one of the most suitable hydrogen energy sources due to high hydrogen content (19.6%), high solubility and stability in water at room temperature [1,2]. Until now, many different types of mono and bimetallic nanoparticle based heterogeneous catalysts were studied for the

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dehydrogenation of ABs due to their smaller size and better catalytic performances [3–6]. Besides, the dehydrogenation of dimethylamine–borane, DMAB, one of the derivatives of ABs, has also been gaining attention as well as other ABs. Further, many different homogeneous and heterogeneous catalysts were tested for dehydrocoupling of DMAB by using metal-based complexes such as Ru, Rh, Pd, and Ir complexes [7], Ru(H)(PMe₃)(PNP) and trans-Ru(H)₂(PMe₃)(PNPH) [8], [Rh(1,5-cod)(μ-Cl)]₂ [9–11], [Cp₂Ti] [12,13], [RuH₂(η²-H₂)₂(PCy₃)₂] and [RuH₂(η²:η²-H₂B-N(Me)₂(PCy₃)₂)] [14], RhCl₃, colloidal Rh/[Oct₄N]Cl and Rh/Al₂O₃ [9], laurate-stabilized Rh(0) [15], hexanoate-stabilized Rh(0) [16], aminopropyltriethoxysilane-stabilized Ru(0) [17], Re complexes [18], Rh₄₋₆ clusters [19], RhCl(PHCy₂)₃ [20], Ru/ZIF-8, [Ru(p-Cym)(bipy)Cl]Cl [21], Pd(0)/MOF [22], Pt(0)/amylamine [23], Pt(0)/TBA [24], Pt(0)@AC [25], Pt(0)@CNT [26]. Although the record activity has been achieved by using homogeneous [η⁵-C₅H₃-1,3(SiMe₃)₂]₂Ti₂ catalyst [27], the current research has focused on the development of new metal nanoparticle catalysts because of their significant advantages in product isolation, catalyst recovery and reusability. In recent years, reduced graphene oxide (rGO) has been shown to be a promising support due to its unique characteristics of high electrical conductivity, large specific surface area and improved durability relative to traditional carbon black [28,29]. Nevertheless, rGO supporting nanocatalysts still face critical issues: (1) irreversibly restacking of rGO sheets resulting from their strong interactions, causing most catalyst nanoparticles to be embedded between rGO layers and unavailable to reactants so that the catalysts are not fully utilized [30]; (2) sintering and dissolution of catalyst nanoparticles because of their high surface energy and weak interactions with rGO supports, deteriorating the activity during fuel cell operation [31]; and (3) carbon corrosion of rGO supports [32,33] disrupting the structural integrity of the catalyst layer and leading to the detachment of catalyst nanoparticles. Various strategies toward solving these problems have been proposed, for example, inserting spaces between rGO sheets [33,34] or self assembly of rGO sheets into porous three-dimensional architectures to prevent rGO stacking [35] and surface treatments of rGO to suppress its carbon corrosion and synchronously stabilize nanoparticles [36–38]; however, the development of a rGO-based catalyst with all of the above issues addressed simultaneously is a great challenge. Herein, we engineer polyaniline (PANI) layer reduced graphene oxide (rGO) nanosheets as a novel support platform for metal nanoparticles. This sophisticated architecture provides a new direction toward solving the potential problems. First, nanostructure can maximally facilitate the mass transport, and meanwhile the supported catalyst particles can expose as many active sites as possible to reaction molecules, ensuring the best utilization of the catalysts. Second, the chemically stable PANI overlays rGO, not only restraining the stacking interactions among rGO sheets but also protecting rGO from direct exposure to the corrosive environment to promote durability. Third, compared to rGO, which usually shows incompatibility with inorganic materials, PANI is also an electrically conductive material and, additionally, it can provide abundant nitrogen atoms to bind with metal ions for facilitating the controllable growth of inorganic/metallic nanoparticles with enhanced anchoring effects. Therefore, the

coupled PANI aligned rGO hybrid nanosheet supported catalysts can be expected to be both highly active and robust in hydrogen systems. Because the chemically derived graphene, namely, rGO, can be obtained massively from low-cost graphene oxide (GO) under mild conditions and, furthermore, can be easily hybridized with other functional materials to create synergistic effects, aligning rGO has been attractive for hydrogen storage applications [39]. However, general and effective strategies for rGO have been scarcely developed. In this study, we report a one-step chemical assembly strategy for preparing rGO via PANI inhibiting the stacking interactions between rGO sheets, obtaining PANI coupled rGO (denoted PANI@rGO) hybrid nanosheets. By taking advantage of the unique chemistry of PANI, Pt nanoparticles could be decorated on PANI through the spontaneous reaction of PANI with selected metal salts. Herein, we addressed to a facile method for the preparation of Pt@PANI-rGO nanocatalysts in the dehydrogenation reaction of DMAB. On the other hand, their excellent catalytic performance was also analyzed. The characterization of the prepared catalyst was also performed by using different analytical techniques such as UV–Vis, XPS, TEM, XRD and HR-TEM analyses and the production of the nanocatalyst was carried out by special method in which both of the metals co-reduced by the ultrasonic double reduction method. The nanocatalysts having noble metal like Pt is known to be expensive, however, their exceptional performances as catalyst takes them to a special position in the compact hydrogen production systems employing DMAB as hydrogen containing compound due to elimination of worries regarding the high catalyst charge.

Experimental methods

Pt nanomaterials stabilized by PANI-rGO production

The Pt@rGO–PANI nanocomposites were prepared by a novel route. In brief, a small amount of reduced graphene oxides dissolved in water by ultrasonic treatment for a couple hours, followed by addition of the same amount of polyaniline and water while stirring for another a couple hours. After that, 0.025 mmol PtCl₄ were added into the these solution. This addition was carried out under ultrasonic conditions. Thereafter, the solution was stirred under reflux at 90 °C for 12 h. Pt@rGO–PANI NPs were reproducibly generated by addition of superhydride. Superhydride addition continued until no H₂ gas bubbled from the solution, indicating a complete reaction. The obtained Pt@rGO–PANI NPs as a precipitate in solution were separated by centrifugation. Consequently, the prepared nanocatalyst was washed several times with ethanol and pure water and dried in a vacuum at room temperature. On the other hand, the same procedure as described above were applied to produce Pt nanoparticles attached on reduced graphene oxides (Pt@rGO) or polyaniline (Pt@PANI) for performance comparison. Analytical investigations, catalytic activity, and reusability performances of the prepared Pt@rGO NPs, Pt@PANI NPs and Pt@PANI-rGO NPs for DMAB dehydrogenation and examination of E_a of monodisperse Pt@PANI-rGO NPs have been analyzed in detail.

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