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International Journal of HYDROGEN ENERGY

Graphite oxide functionalized with ionic liquid and ruthenium as hydrogenation catalyst

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ARTICLE INFO

ABSTRACT

The manuscript herein is on the synthesis and characterization of a graphene composite abbreviated as GO-IL-Ru that is based on graphite oxide with additional functional groups of organic ionic trains. It contains Ru at 1.61 wt% level (by ICP-OES). We have used GO-IL-Ru as catalyst in both the hydrogenation reactions and the transfer hydrogenation reactions. The catalytic activity of GO-IL-Ru was good at compounds with phenyl groups, but not at those containing electronegative substituents or heterocyclic rings.

1. Introduction

Graphene, the single layer graphite, is one of the most popular research targets nowadays. Professors Geim and Novoselov published the developments about graphene in 2004 [1]. And the field was recognized with the Nobel Prize at 2010. Graphene sheets offer high carrier mobility at room temperature ($\sim$10,000 cm^2 V^{-1} s^{-1}) [1], large theoretical specific surface area (2630 m^2 g^{-1}) [2], good optical transparency ($\sim$97.7%) [3], high Young's modulus ($\sim$1 TPa) [4] and excellent thermal conductivity (3000—5000 W m^{-1} K^{-1}) [5,6].

Taking advantage of its convenience and low-cost in mass production, scientists focus on chemically exfoliated graphite oxide (GO) and reduced graphene oxide (rGO). Although after reduction, the latter still contains to some extent the oxygen functional groups on the surface. These additional oxygen groups could bring in further modifications such as metal nanoparticles [7—10], polymers [11], biomaterials [12,13]. Graphene composites are expected to find a variety of applications in, such as chemical sensing [12], battery electrode [14], super capacitor [10,15], and hydrogen storage [16].

More recently, scientists have come to agree that hydrogen energy is the answer to the ever increasing demand and to the reduction of greenhouse effect [17,18]. Hydrogen production is important. But hydrogen as a gas, is hard to compress, and is also dangerous material during transportation. Alternatively a hydrogenation and dehydrogenation loop equals to a hydrogen storage chemically [19]. These processes could avoid the highly explosive probability of hydrogen gas, during the storage and transportation.

Ruthenium is interesting when viewing at its strong catalytic activities in hydrogenation reactions [20—22] and in transfer hydrogenation reactions [23,24]. Its catalysis is generally under very mild conditions [22]. In this study, we

have attempted to use the Ru-graphene composite as the hydrogenation and as the transfer hydrogenation catalyst.

2. Experimental section

2.1. Chemicals and instruments

Chemicals were bought from Aldrich and Alfa Aeser and used directly without further purification. XRD data were from PANalytical X'Pert Pro MPD powder X-ray diffractometer with Cu Kα radiation at 50 kV and 40 mA. The scanning rate was 0.625°/min and the 2θ range 5–80°. The samples for FT-IR analysis were measured with Perkin Elmer spectrum 100 and Miracle ATR Accessory. Samples were scanned from 400 to 4000 cm^{-1} with resolution at 0.01 cm^{-1} for 60 min accumulation of signals. Physical Electronics PHI Quantra XPS microprobe equipped with Al Kα monochromatic X-ray source (25.3 w, 45° incident angle and 280 eV) was employed for X-ray photoelectron spectroscopy (XPS) analysis on GO-IL-Ru. NMR data were measured from Bruker AVA-500 (500 MHz), AVA-400 (400 MHz) and AVIII-400 (400 MHz). ICP-OES data was measured from Agilent Technologies 720-ES. SEM images were measured from Zeiss Ultra Plus.

The Ru K-edge X-ray absorption fine structure spectra (XAFS), including X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structural spectra (EXAFS), were recorded with beamline BL01C1 at the National Taiwan Synchrotron Radiation Research Center (NSRRC) in fluorescence mode for powdered samples. The electron storage ring was operated at 1.5 GeV with a current of 120–200 mA. A Si (111) double-crystal monochromator was used for the selection of photons with a specific energy. The characteristic pre-edge absorption of a Ru foil at 22117 eV was used for the calibration of energy shifts [25]. The Ru-EXAFS data were analyzed using the analytical package "Artemis". Fourier transformation was carried out on k^3-weighted EXAFS oscillations at 2.516–12.578 $Å^{-1}$.

2.2. Preparation of the catalysts

The graphite oxide (GO) synthesis followed the modified Hummer's method [26]. Fuming sulfuric acid (25 mL) was poured into a 250 mL round bottomed flask at iced bath, followed by introduction of nitric acid (10 mL) in 15 min. Using an iced bath, graphite powder (1 g) was added into the flask with intensive stirring. After the mixture was well dispersed, potassium chlorate (22 g) was added into the flask in 30 min. Then, the ice bath was removed and the solution stirred at room temperature for 96 h. The solution was added with D. I.(= deionized) water at an iced bath, then the mixture was centrifuged together with D. I. water for three times to remove all aqueous ions. The graphite oxide slurry was then washed with methanol to remove water and dried under vacuum.

1-Methyl imidazole (26.0 g) and 3-chloropropyl ammonium chloride (47.5 g) were added in a 250 mL flask with 100 mL ethanol. The solution was then refluxed at 80 °C overnight before the reaction was stopped. The solution was then cooled to room temperature and applied with vacuum to remove ethanol. The room temperature ionic liquid N-(3-aminopropyl)-N′-methylimidazolium chloride HCl salt [MPIm][Cl] (see Fig. 1) was formed and tested with ^{1}H NMR (400 MHz, D_2O @ δ4.8 ppm) [27,28]. δ(ppm): 8.82(s, 1H, N−CH = N); 7.56 (s, 1H, N−CH = CH−NCH₃); 7.48 (s, 1H, N−CH = CH−NCH₃); 4.35 (t, 2H, N−CH₂−CH₂-); 3.90 (s, 3H, −N−CH₃); 3.17 (t, 2H, N−CH₂−CH₂−CH₂−NH₃⁺); 2.30 (t, 2H, N−CH₂−CH₂−CH₂−NH₃⁺).

GO (4.0 g), [MPIm][Cl] (16.0 g) and KOH (8.0 g) were added into a 250 mL flask with water (150 mL) and sonicated for 30 min to make sure that all the GO powders were well dispersed in water. The solution was refluxed at 100 °C overnight, and then cooled to room temperature before being centrifuged with D. I. water three times to remove all the aqueous ions, which is followed by washing with methanol to remove water then drying under vacuum. The slurry of graphite oxide composite (GO-IL) was formed [28].

RuCl₃ 3H₂O (330 mg) and ethanol (40 mL) were sonicated in a 100 mL flask for 30 min. Then the solution was transferred into a 250 mL stainless steel reactor. The reactor was then assembled and filled with hydrogen (140 psi) at room temperature [29]. After stirring for 48 h, the product solution Ru/EtOH was mixed with GO-IL (4.0 g) in a 100 mL flask and treated with ultra sonication for 30 min. The solution was then vacuumed to remove EtOH, and the composite GO-IL-Ru was formed.

For ICP-OES analysis, 50 mg of GO-IL-Ru was heated at 500 °C under oxygen for 1 h with the oxygen flow rate at 1 mL s^{-1}. After annealing, the remaining powder was dissolved in HNO₃ (10 mL). The solution was then heated in a microwave reactor with 80 W at 120 °C for 1 h. The solution was then diluted to 100 mL with D. I. water for ICP-OES test. A total of 5 samples were repeated in a similar manner to yield the reported average weight percentage of Ru.

1-Methyl imidazole (20.0 g) and 1-chlorobutane (23.0 g) were added in a 250 mL flask with 100 mL ethyl acetate. The solution was then refluxed at 80 °C overnight. After the reaction, the solution was cooled to room temperature and the ionic liquid layer separated from the organic layer. The ionic liquid layer was washed by ethyl acetate (50 mL) three times to remove the remaining reactants. The washed ionic liquid was then vacuumed to remove organic volatiles. Methyl n-butyl imidazolium chloride [BMIm][Cl] was formed and characterized with ^{1}H NMR (400 MHz, D_2O @ δ4.8 ppm) [27,28]. δ(ppm): 8.92 (s, 1H, N−CH = N); 7.65 (s, 1H, N−CH = CH−NCH₃); 7.60 (s, 1H, N−CH = CH−NCH₃); 4.32 (t, 2H, N−CH₂−CH₂-); 4.0 (s, 3H, −N−CH₃); 1.93 (m, 2H, N−CH₂−CH₂−CH₂−CH₃); 1.39 (m, 2H, N−CH₂−CH₂−CH₂−CH₃); 0.98 (t, 3H, N−CH₂− CH₂−CH₂−CH₃).

Ru/EtOH, the hydrogenated product solution from RuCl₃ in ethanol as described previously (10 mL, contains Ru
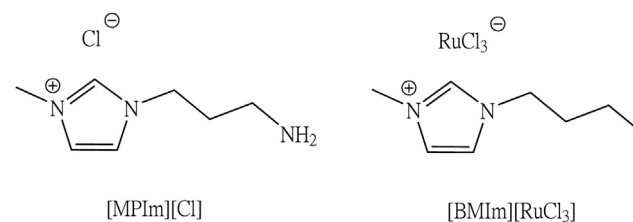

Fig. 1 − **The molecular structure of [MPIm][Cl] and [BMIm] [RuCl₃].**