Selective 1,3-butadiene hydrogenation by gold nanoparticles on novel nano-carbon materials

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ABSTRACT

Graphene oxide and multiwall carbon nanotubes were chemically modified by treatment with an aniline derivate or by incorporating nitrogen-adatoms. These materials were used as supports for gold nanoparticles and the resulting catalytic materials have been applied as catalysts in the 1,3-butadiene hydrogenation reaction. Supports and catalysts were exhaustively characterized by chemical analysis, X-ray photoelectron spectroscopy, thermogravimetric studies, temperature programmed desorption and transmission electron microscopy. The incorporation of nitrogen groups on surfaces modifies the gold precipitation–deposition process, giving place to different nanoparticle sizes and amounts of gold. From the point of view of catalytic behaviour an unusual activity for 1,3-butadiene was obtained with the gold amine functionalized graphene catalyst. The gold nanoparticles supported on graphene modified by p-phenylenediamine are more active than when supported either in the other samples. In particular, gold supported on graphene modified with amine like groups becomes active at near ambient temperatures, which is unusual for gold catalysts. Especially interesting is the variation of the gold catalytic properties, after recycling experiments.

1. Introduction

Among the numerous carbon materials, graphite oxide (GO) or carbon nanotubes (CNT) exhibit many outstanding properties. These properties (physical, chemical and mechanical) allow the preparation of composite-materials with unprecedented characteristics [1]. The incorporation of reduced GO (graphene) or CNTs into the composite-materials can offer unique properties and possibly induce new functions based on synergetic effects.

The GO material can develop an interesting chemistry when used as catalyst support, allowing intercalation not only by ionic exchange but also by covalent bonding through the acidic hydroxyl groups on its layers at the time they expand opening the pore structure giving way to composite-materials. Frequently, the second component of theses composites can be a metal, and in such a case it is possible to adjust the metal-support interaction by modifying the functionalities of the graphenic surfaces. Among others methods to engineer the electronic structure of graphene, synthesis methods,

chemical functionalization of graphene and chemical doping are the most outstanding. One common technique to produce nano-hybrid graphene composites consists in anchoring nanoparticles (NPs) onto GO sheets, where functional groups act as nucleation centres. This allows a covalent bond of the metal to the basal plane of graphene, yielding high dispersions. Then, graphene oxide and the metal precursor can be chemically reduced to form the corresponding graphene–metal composite. Another interesting way to provide a new generation of catalysts is to develop the confinement effects in the nanospace between the GO layers via intercalation [2]. This effect was also studied in the inner cavity of carbon nanotubes (CNTs) [3,4].

CNTs may be viewed as cylindrical structures formed from graphene sheets and closed or not by hemispherical caps at each end. They are hollow nano-sized tubes and their nanometrical dimensions, together with the unique electronic structure of the graphene sheet, make the electronic properties of these one-dimensional structures very interesting. In the case of CNTs, chemical processes can be used to tailor the carbon porous structure and the type and concentration of specific surface groups. A wide variety of oxidizing treatment techniques have been applied to functionalize the carbon surface. Further modifications of carbon
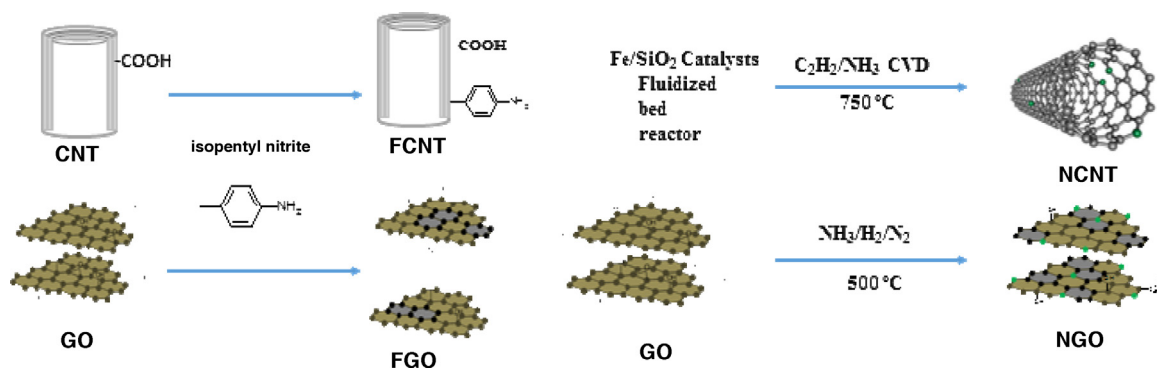
Scheme 1. Procedure for catalysts preparation.

surfaces with other functionalities containing heteroatoms, like N and S, tend to increase their chemical reactivity for subsequent chemical modifications such as the anchoring of metal complexes to the support.

Supported gold catalysts with high dispersed nanoparticles in the size ranged from 1 to 10 nm have been reported highly active/selective for a number of reactions [5]. The contact surface, support selection and particle size were reported key factors in determining the catalytic performance of supported gold catalysts. Then modified GO and CNTs show potential applications as a new group of gold-composite materials, owing to their enhanced properties in catalysis.

In the present paper we report an efficient methodology to incorporate amine groups or nitrogen-adatoms onto GO or CNTs structures, permitting changes in the support properties. A deposition–precipitation synthetic procedure was used to incorporate gold on functionalized and nitrogen-doped carbon supports in order to design high-performance gold catalysts. We present the results of catalytic performances in the 1,3-butadiene (BD) selective hydrogenation towards alquenes (butene, tras-2-butene, cis-2-butene) of gold supported on layer graphene composite and on multi-walled carbon nanotubes. This work also reports a striking enhancement of catalytic performance of gold nanoparticles (NPs) on the functionalized graphene surface, after successive reaction cycles.

2. Experimental

2.1. Preparation of materials

Different types of nano-carbon materials were used in this study: functionalized graphite oxide (FGO), nitrogen-doped GO (NGO), functionalized CNTs (FCNT) and nitrogen-doped CNTs (NCNT). All samples were prepared in our laboratory. In a first step GO was synthesized from natural graphite powder (99.999% stated purity, 100 mesh) following a modification of the Brodie's method [6,7]. Briefly the graphite was added to a reaction flask containing fuming HNO_3 (20 mL/g of support), which was previously cooled to 0 °C in an iced bath, after that potassium chlorate was slowly added. The reaction was left to proceed for 21 h under stirring, and the final solid was filtered, extensively washed with deionized water until neutral pH, and dried under vacuum at 323 K overnight. In order to functionalize the GO by diazonium grafting chemistry [8], the GO was dispersed in DMF with sonication during 10 min. p-Phenylenediamine was added to the reaction medium which was left under argon and heated to 80 °C. Then, isopentyl nitrite (radical initiator) was added to the reaction slowly, in a molar ratio of 0.5 to p-phenylenediamine. The reaction mixture was kept under stirring for 48 h and the resulting material was denoted as FGO. Nitrogen doped GO was synthesized in a fluidized

bed reactor from GO and nitrogen-hydrogen-ammonia mixture with flow rates of 10, 6 and 50 mL/min at 300 °C obtaining NGO [7].

CNT_s were synthetized and characterized in our laboratory in previous works [9]. These CNTs were further oxidized by nitric acid at 120 °C for 3 h and functionalized by same procedure carried out for the FGO synthesis. The obtaining sample was labelled FCNT. Finally, nitrogen-doped nanotubes NCNT were produced by catalytic chemical vapor deposition in a fluidized bed reactor on Fe/SiO₂ catalysts from acetylene-ammonia mixtures at 750 °C. These CNT_N were characterized in our previous works and they presented a bamboo-like structure with graphene layers perpendicular to the CNT axis [10].

2.2. Preparation of catalysts

Deposition–precipitation method was used in order to synthesize the gold catalysts. A solution of [$HAuCl_4$] was added to the selected carbon support. After ultrasonic treatment at 283 K for 5 min, it was treated with a water solution of Na_2CO_3 (0.1 M) until pH = 11. Then, the precipitate was stirred for 5 h and collected by filtration. Finally, the precipitate was washed with deionized water, until no Cl^- was detected. The sample was dried overnight at 373 K in air. The corresponding catalysts were labelled AuFGO, AuNGO, AuFCNT and AuNCNT. These samples were subjected to a pretreatment in flowing H_2 at 250 °C for 1 h previous to the hydrogenation reaction tests. Scheme 1 summarizes the experimental procedure for the preparation of the catalytic systems.

2.3. Physical–chemical characterization and catalytic measurements

The support samples were characterized by X-ray photoelectron spectroscopy (XPS), thermogravimetric analyses, temperature programmed desorption experiments and transmission electron microscopy (TEM). XPS analysis was performed with an ESCA-PROBE P (Omicron) spectrometer by using nonmonochromatized Mg-K radiation (1253.6 eV). Thermogravimetric analyses (TGA) were conducted under nitrogen in a TA instruments, model SDT Q600 TA System. The sample (~5 mg) was placed in a platinum crucible and heated with a 10 °C min⁻¹ ramp between 298 and 1273 K, followed by an isotherm at that temperature for 30 min. The chemical nature of the surface functional groups was evaluated by temperature programmed desorption coupled with mass spectrometer (TPD-MS). These experiments were performed under vacuum in a conventional volumetric apparatus connected to a RGA-200 SRS mass spectrometer [11]. The sample was evacuated for 30 min at room temperature and then ramped to 1023 K at a 10 K min⁻¹ rate. To obtain the point of zero charge (PZC), the electrophoretic mobility (μ) vs. pH of the samples were measured in