



Nanodiamond decorated few-layer graphene composite as an efficient metal-free dehydrogenation catalyst for styrene production



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ABSTRACT

Hybrid materials consisting of graphene and nanodiamonds (NDs) can potentially display not only the individual properties of ND and graphene, but also those resulting from synergism when they closely interact. Herein, synergistic effects between ND and few-layer-graphene (FLG) containing between 5 and 20 layers of graphene are examined. The ND/FLG composite was prepared by mixing a suspension of FLG in ethanol with NDs. In this case, FLG plays the role of 2D support for dispersing ND clusters while NDs acting as a nano-spacer for partly preventing the re-stacking of the FLG sheets. The as-synthesized hybrid material was further used as metal-free catalyst for the steam-free direct dehydrogenation (DH) of ethylbenzene (EB) to styrene (ST). The DH activity obtained on the ND/FLG catalyst was benchmarked with other catalysts, i.e. commercial K-promoted Fe-based catalysts and carbon-based catalysts. The ND/FLG catalyst exhibits the highest DH activity among the tested catalysts, especially with a dehydrogenation specific rate as high as $19 \text{ mmol}_{\text{ST}} \text{ g}_{\text{ND}}^{-1} \text{ h}^{-1}$ along with a selectivity toward styrene up to 95% at reaction temperature at 600 °C. The catalyst displays a relatively high stability as a function of time on stream while the deactivated catalyst can be easily regenerated by an oxidative treatment in mild temperature conditions.

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1. Introduction

Styrene is well recognized as one of the most important monomers for polymers and copolymers synthesis. Its production has known an exponential growth during the past century and will own this position for a long time to come. The industrial process for the catalytic dehydrogenation of ethylbenzene to styrene is one of the 10 most important organic catalytic processes [1]. Over 25×10^6 tons/year of styrene monomer is produced worldwide [2] which are further used in different types of application, including raw materials for the production of polystyrene, synthetic rubbers, plastics, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins.

Styrene is mostly produced by direct dehydrogenation of ethylbenzene on an iron-based catalyst, generally promoted with alkaline. Due to the endothermic character and

equilibrium limitations of the dehydrogenation reaction, high temperatures are usually needed (i.e. 500–700 °C). In such temperature conditions a large amount of carbonaceous is stepwise deposited on the iron surface during the reaction leading to a gradual encapsulation of the active phase and subsequent deactivation [3]. The presence of steam in large excess in the ethylbenzene dehydrogenation can partly remove the carbonaceous deposition by the gasification reaction and then preserve the catalyst activity. Steam also provides heat to maintain the reaction temperature within the catalyst bed in order to counter balance the endothermic character of the process. However, this process has a significant drawback since high energy consumption is required corresponding to 1.5×10^9 cal/ton of styrene [4]. In order to overcome this problem, oxidative dehydrogenation has been proposed as an alternative catalytic route.

Numerous studies have been focused on the low-temperature oxidative dehydrogenation (ODH) of ethylbenzene into styrene [5–8]. Indeed, during the last decade, metal-free catalysts based on nano-carbon materials, i.e. carbon nanotubes, either pure or doped, and carbon nanofibers, have been reported to be an alternative route for performing the oxidative dehydrogenation (ODH) of ethylbenzene to styrene [9–11]. The high degree of

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graphitization of these materials allows them to survive harsh operation conditions which would damage activated carbon due to its lower oxidative resistance [10,11]. It is worthy to note that a large part of the literature data deals with the use of these metal-free nano-carbon catalysts in the oxidative dehydrogenation of alkanes in the presence of oxygen (ODH) while the direct dehydrogenation is only scarcely reported. In fact, the ODH reaction presents some important disadvantages compared to the oxygen-free dehydrogenation process namely the use of a mixture containing oxygen and hydrocarbon which leads to low selectivity toward styrene formation due to parallel side-reactions such as combustion. Recently, a report emphasized the use of nanodiamonds-based catalysts in the oxygen- and steam-free dehydrogenation of ethylbenzene to styrene [12]. It was found that nanodiamonds (NDs) catalyst exhibits a relatively high DH activity compared to that obtained on an iron-based commercial catalyst, i.e. 20.5% of EB conversion instead of 7.1%, and an almost exclusive selectivity toward styrene, i.e. 97%, and a long-term stability up to several tenth of hours on stream [12]. The NDs also display an extremely high DH activity compared to other carbon-based catalysts as reported elsewhere [12]. The high DH activity of the NDs was attributed to the presence of a core-shell structured material, i.e. NDs wrapped with graphene layer with a unique sp^2 – sp^3 hybrid structure, which provides high activity related to a partial delocalization of the electron density. The sp^2 – sp^3 hybrid structure of NDs also actively contributes to the reduction of coke formation on the carbon surface [13]. However, commercial NDs in a powder form are composed of agglomerates which significantly reduce the accessibility of the active sites. Recently Su and co-workers [14] prepared NDs supported on a composite constituted by a silicon carbide host structure decorated with carbon nanotubes. The carbon nanotubes play the role of high effective surface support to anchor the NDs compared to the relatively low specific surface area of the SiC host structure which can hardly disperse the NDs.

The aim of the present study is to develop a highly active carbon-based catalyst consisting of dispersed nanodiamonds (NDs) decorated few-layer graphene (FLG) for the steam-free dehydrogenation (DH) of ethylbenzene (EB) to styrene (ST) in a fixed-bed reactor configuration. Few-layer graphene contains a large number of vacancies and defects which can promote the dispersion of NDs particles. Previous works has shown that the FLG is an efficient support for palladium in the liquid-phase hydrogenation of cinnamaldehyde [15]. In this present work, the dispersion of the NDs on the FLG surface leads to an increase of the density of active sites and, as a consequence, a significant improvement in the DH activity compared to bulk NDs while keeping the selectivity toward ST unchanged. The catalyst displays a higher DH performance compared to that obtained on the commercial iron-based catalyst which highlighted the advantage of using carbon-based catalysts to replace metal oxide catalysts for such a highly demanded reaction [16]. The as-synthesized catalyst also exhibits an extremely high stability as a function of the experiment duration.

2. Experimental

2.1. Nanodiamonds and few-layer graphene characteristics

The commercial nanodiamonds in powder form were supplied by the Hightech Co (Finland) and were used without any further purification. The NDs size, measured by TEM, was centered at around 5 ± 2 nm and is present in large aggregates (Fig. 1A and D).

The FLG was synthesized by sonication of the expanded graphite (EG) at room temperature in an ethanol medium. The sonicated sample was allowed to settling for 30 min and the supernatant suspension containing thin few-layer graphene sheets was recovered

for subsequent use. TEM analysis shows that the FLG is characterized by a large lateral size up to several micrometers and contains between two up to twenty graphene layers (Fig. 1B and E). High-resolution TEM analysis indicates the presence of vacancies and defects on the FLG surface which provide anchorage sites for the active phase dispersion and stabilization. However, Raman analysis indicates that the FLG produced from the exfoliation of the expanded graphite used in this work is more graphitized and contains a lower number of defects than its counterpart synthesized by a mechanical ablation or sonication process of graphite-based materials [17].

2.2. Synthesis of the ND/FLG catalyst

The suspension of FLG (typically from 5 to 20 layers) in ethanol was mixed with NDs through sonication process at room temperature for 1 h. The sonication allowed de-staking of the graphene sheets from each other because graphene has a high tendency to re-stack leading to a small exposed surface area. The formed mixture was then dried under agitation until the complete evaporation of solvent leading to the formation of the ND/FLG composite. The as-synthesized catalyst was further annealed in argon flow at 900°C for 2 h before catalytic measurements in the direct dehydrogenation process. The NDs particles were anchored on both sides of the FLG sheet, according to our previous investigations of the Fe_3O_4 /FLG system by TEM tomography [18,19] preventing further excessive re-stacking of the FLG sheets in the final composite.

2.3. Characterization of techniques

X-ray diffraction (XRD) measurements were carried out in a Bruker D-8 Advance diffractometer equipped with a Vantec detector ($\text{Cu K}\alpha$ radiation). The powdered sample was packed onto a glass slide. The data sets were acquired in step-scan mode in a 2θ range 10 – 80° .

The scanning electron microscopy (SEM) was carried out on a JEOL 2600F with a resolution of 5 nm. The sample was deposited onto a double face graphite tape in order to avoid charging effect during the analysis.

The TEM analysis was carried out on a JEOL 2100F working at 200 kV accelerated voltage, equipped with a probe corrector for spherical aberrations, and a point-to-point resolution of 0.2 nm. The sample was dispersed by ultrasounds in an ethanol solution for 5 min and a drop of the solution was deposited on a copper covered with a holey carbon membrane for observation.

The specific surface area of the support and the catalyst, after reduction, were determined in a Micromeritics sorptometer. The sample was outgassed at 250°C under vacuum for 8 h in order to desorb moisture and adsorbed species on its surface. Physisorption measurements were carried out using N_2 as adsorbent at liquid N_2 temperature at relative pressures between 0.06 and 0.99.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW ClassWA hemispherical electron analyzer. A monochromated $\text{Al K}\alpha$ X-ray source (1486.6 eV) was used as incident radiation and XP spectra were recorded using pass energy of 20 eV. Survey and high resolution spectra were recorded in constant pass energy mode (100 and 20 eV, respectively). The CASA XPS program with a Gaussian–Lorentzian mix function and Shirley background subtraction was employed to deconvolute the XP spectra.

2.4. Selective dehydrogenation of ethylbenzene to styrene

The steam-free catalytic dehydrogenation of ethylbenzene to styrene was carried out in a fixed-bed continuous flow reactor at

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