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Structure-performance relationship of nanodiamonds @ nitrogen-doped mesoporous carbon in the direct dehydrogenation of ethylbenzene

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ABSTRACT

Nanocarbon materials have been reported as an alternative robust metal-free catalyst in the field of the catalytic dehydrogenation with improved catalytic performance as well as stability. In this study, the hybrid metal-free catalyst consisting of dispersed nanodiamonds within a nitrogen-doped mesoporous carbon (ND@NMC) phase was investigated. Such material with high effective surface area and porosity was prepared under different thermal treatment temperatures and further evaluated for the direct dehydrogenation (DDH) of ethylbenzene (EB) to styrene (ST). The characterization techniques such as N_2 adsorption-desorption, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy and Raman spectroscopic analysis were used to investigate the surface properties and structures of the as-prepared ND@NMC composites. The ND@NMC-700 catalyst annealed at 700 °C presented a ST specific reaction rate and a relative areal activity of 5.8 $\text{mmol}_{ST}\ \text{g}_{catalyst}^{-1}\ \text{h}^{-1}$ and 0.28 $\mu\text{mol}_{ST}\ \text{m}^{-2}\ \text{h}^{-1}$ with a ST selectivity of 99.6%, which is the highest DDH activity among the investigated nanocarbons including ND, carbon nanotubes, NMC and ND@MC (ND covered by mesoporous carbon) catalysts. The superior dehydrogenation performance could be attributed to the high dispersion of the metal-free nanodiamond centers within the NMC layer which provided a well surface contact with the reactant. It can also be confirmed that the rational contents of ketone (C=O) functional groups, as well as the opened porous network in ND@NMC-700 catalyst resulted to the superior DDH activity and styrene selectivity. Moreover, the presented nitrogen groups are beneficial for construction of surface defects and porosity as well as the improvement of styrene selectivity.

1. Introduction

Carbon nanomaterials (such as carbon nanotubes/nanofibers, graphene, nanodiamonds, and the related nanocarbons doped with heteroatoms) presenting unique structural features and chemical properties, have been widely investigated in the last decades in various important catalytic processes [1–10]. Among the series of carbon nanomaterials, the detonation nanodiamond (ND), a typical sp^3-hybridized carbon nanoparticle with an average size less than 10 nm, has attracted significant interests as a catalyst support or directly as an effective metal-free catalyst [11–18]. It was reported that ND could be considered as an alternative metal-free catalyst for the production of styrene through the direct dehydrogenation (DDH) of ethylbenzene (EB) [12]. Su and co-workers [12] have shown that nanodiamond presented superior dehydrogenation activity than other carbon nanomaterials, i.e. carbon nanotubes, nanographite and mesopurous carbon in the DDH ethylbenzene reaction to produce styrene, and exhibited DDH activity about three times higher than the one obtained with the iron-based industrial catalyst with similar selectivity towards styrene formation. When the surface of NDs is modified by nitrogen [18] or coated by a layer of carbon nitride hybrid [19,20], the catalytic activity on those modified NDs could be enhanced significantly. It has been demonstrated that the incorporation of nitrogen(s) in the carbon matrix network gives rise to an electronic modification of the adjacent carbon

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atoms leading to unexpected adsorption properties and also increases the catalytic sites through inducing strain and defect sites and, as a consequence, thus improved the catalytic performance and stability [21].

The detonation nanodiamonds possesses the typical diameter around 4–10 nm, however, samples in powder form always tend to aggregate and result to the formation of clusters with size up to hundreds nanometers [11,14], which dramatically decreases the overall active sites. Thus, it is of interest to improve the dispersion of the NDs particles, which would increase the effective contact surface area and the number of active sites per catalyst weight, leading to an enhancement of their catalytic properties. More recent hybrid materials consisting of ND particles uniformly dispersed onto a 2D graphene oxide and few-layer-graphene (FLG) lead to a significant improvement of the DDH activity, which are 1.7 and 3.4 times higher than the bulk nanodiamonds [13,22]. However, the ND is used in powder that easily lead to a significant pressure drop along the catalyst bed and also difficulty for handling and transport [23]. Thus, the ND aggregates are further anchored on the macroscopic shaped carbon nanotubes (CNTs) decorated SiC [24] or porous β-SiC foam [23], in which case the efficient and easy-handled monolith catalyst containing the ND with high dispersion can be obtained. Moreover, we recently reported new synthesis method for preparing highly dispersed nanodiamonds within a nitrogen-enriched mesoporous carbon (NMC) composites based on the use of non-toxic, food-grade components such as ammonium carbonate (leavening agent), dextrose and citric acid [25,26]. The reported monolith ND@NMC/SiC composite presented excellent ethylbenzene dehydrogenation activity at low ND mass loading, even under the severe reaction conditions (600 °C and up to 10 vol.% of EB on stream) [26], suggesting it an ideal candidate of metal-free catalyst for the industrial exploitation of direct dehydrogenation of EB. However, the relationship between their physicochemical properties and the DDH catalytic performance based on such kind of catalyst system (specially the ND@NMC active phase) has not been depicted in detail.

In this study, the nitrogen-enriched mesoporous carbon (NMC) covered ND composites were prepared under different thermal treatment temperature and evaluated for the ethylbenzene DDH reaction. For comparison, the mesoporous carbon wrapped ND was also prepared through the similar process just without nitrogen doping. The characterizations such as N_2 adsorption-desorption, X-ray photoelectron spectroscopy (XPS), High-resolution transmission electron microscopy (HR-TEM) and Raman spectroscopic analysis (Raman) are involved to analysis in details the ND@NMC composites, in order to understand the structure-performance relationship in the DDH reaction.

2. Experimental

2.1. Catalyst preparation

The nanodiamonds (ND) were purchased from the Carbodeon Ltd Oy (Finland) and were used without any further treatment. The ND-700 and ND-900 samples were produced by annealing of the commercial ND at 700 and 900 °C for 2 h in helium atmosphere, respectively. The fabrication of ND@NMC was illustrated in Fig. 1. In a typical procedure, D-Glucose (2 g) and citric acid (3 g) were added in 10 mL of ultrapure Milli-Q water at room temperature. A proper amount of ammonium carbonate (3 g) was then added in one portion to the solution at room-temperature (r.t.) and an instantaneous effervescence was observed due to CO_2 formation. Then 2 g of ND aggregates were added by the assistance of sonication process at room temperature for 20 min. The obtained mixture was directly moved into an oven and treated at 130 °C for 5 h. The solids were further thermal treated in air flow at 400 °C (2 °C min^{-1}) for 2 h during, and then were annealed in helium atmosphere at 700 or 900 °C (10 °C min^{-1}) for 2 h in order to increase the graphitization/conjugation degree of the final materials. The final samples were marked as ND@NMC-700 and ND@NMC-900, respectively. For comparison, the same method was used just without ammonium carbonate addition for preparing ND@MC and finally treated in helium at 700 or 900 °C. The as-prepared samples were named as ND@MC-700 and ND@MC-900. The ND-free sample was prepared following by the same process and noted as NMC-700.

2.2. Characterization techniques

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 the problem of charging effect during the analysis. The N_2 adsorption-desorption measurement for carbon hybrid materials was determined in a Micromeritics sorptometer. The sample was outgassed at 250 °C under vacuum for 14 h in order to desorb moisture and adsorbed species on its surface. The average pore size was calculated based on Barrett-Joyner-Halenda (BJH) algorithm method using the desorption branch. The total pore volume was derived from the amount of gas adsorbed at a relative pressure close to unity, by assuming that the pores were then filled with condensed adsorptive in the normal liquid state. The Raman analysis was carried out using a LabRAM ARAMIS confocal microscope spectrometer equipped with CCD detector (325 nm and 532 nm). A laser line was used to excite sample, 532 nm/100 mW (YAG) with Laser Quantum MPC600 PSU. X-ray diffraction (XRD) measurements were carried out with a θ/2θ mode in a Bruker D-8 Advance diffractometer equipped with a Vantec detector. The TEM analysis was carried out on a FEI Tecnai G2 microscope with an accelerating voltage of 120 kV, equipped with a probe corrector for spherical aberrations, and a point-to-point resolution of 0.2 nm. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer with an Al Kα (1486.6 eV, 15 mA) X-ray source. The C1s peak at 284.6 eV was used to correct charging effects. Shirley backgrounds were subtracted from the raw data to obtain the areas of the C1s peak.

2.3. Catalytic dehydrogenation experiment

The steam-free, direct catalytic dehydrogenation of ethylbenzene for the production of styrene was carried out in a fixed-bed continuous flow quartz reactor under atmospheric pressure. 150 mg of catalyst was loaded onto a quartz fritted disk located inside a tubular quartz reactor (id × L: 8 mm × 800 mm). Helium gas was fed into the reactor at a flow rate of 30 mL min^{-1} through a mass flow controller (BROOKS MFC) and passed through a glass evaporator filled with liquid EB maintained at 40 °C (EB partial pressure of 2.922 kPa) using a thermal regulated bath. The helium flow containing EB was passed downward through the catalyst bed.

The reaction system was heated to 550 °C and kept for 2 h under helium flow. The reactant flow (2.8 vol.% EB diluted in helium, total flow rate of 30 mL min^{-1}) was then fed into the reactor at 550 °C. The reactant and the products (styrene (ST), benzene (BZ) and toluene (TOL)) exited from the reactor was analyzed on-line with a PERICHROM (PR 2100) gas chromatography equipped with a flame detector (FID) and CP WAX S2CB column which were previously calibrated. In order to avoid any possible condensation of the reactant or the products all the tube lines were wrapped with a heating wire kept maintaining 110 °C.

The ethylbenzene conversion (X_{EB}) and styrene selectivity (S_{ST}), as well as styrene formation rate in terms of mass ($\lambda_{catal.}$) and specific surface area (λ_{SSA}) of the catalysts were evaluated using Eqs. (1)–(4):

$$X_{EB}\,[\%] = (1 - \frac{FC_{EB,outlet}}{F_0 C_{EB,inlet}}) \times 100 \tag{1}$$

$$S_{ST}\,[\%] = \frac{C_{ST,outlet}}{(C_{ST,outlet} + C_{TOL,outlet} + C_{BZ,outlet})} \times 100 \tag{2}$$