C. R. Chimie 19 (2016) 1303–1309

Contents lists available at ScienceDirect

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Nitrogen-doped carbon nanotube spheres as metal-free catalysts for the partial oxidation of H_2S

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ARTICLE INFO

Article history:
Received 30 June 2015
Accepted 8 September 2015
Available online 4 March 2016

Keywords:
Nitrogen-doped carbon nanotubes
Macroscopic shape
Metal-free catalyst
Desulfurization
H_2S oxidation

ABSTRACT

Nitrogen-doped carbon nanotubes (N-CNTs) with macroscopic shaping were synthesized by a coagulation route using alginate as a coagulating agent and the as-synthesized sample was used as metal-free catalysts in the partial oxidation of H_2S into elemental sulfur. The N-CNT beads display a relatively high desulfurization activity along with a high stability as a function of time on stream. The desulfurization performance of the N-CNT beads was also measured and compared to that of the Fe_2O_3/SiC catalyst. The N-CNT beads display a higher desulfurization activity under the similar reaction conditions with, however, lower sulfur selectivity due to the problem of diffusion of the reactant through the bead porosity.

1. Introduction

Nitrogen-doped carbon nanotubes (N-CNTs) have received an ever growing scientific interest during the last few decades for their high catalytic performance in several relevant catalytic processes compared to the traditional metal and oxide supported catalysts [1–6]. According to the recent literature survey the catalytic processes involving N-CNTs are continuously expanded with time and part of the results obtained is summarized in some recent reviews [7–10]. The atomic dimensions of carbon, nitrogen and oxygen as well as the bond length in aromatic structures do not differ very much which makes the latter two elements very suitable for incorporation into the CNT matrix. However, the C—N bond is shorter as compared to the C—C and C—O bond lengths. Therefore, incorporation of nitrogen into the carbon matrix may distort a perfectly ordered graphitic matrix leading to possible modification of the overall electronic properties of the material and thus, its catalytic activity.

However, the use of N-CNTs also represents some drawbacks due to its nanoscopic dimension which could pose serious problems for its handling and transport and also for its use in industrial catalytic reactors. Indeed, N-CNTs can be used as such in their nanoscopic shape in the Oxygen Reduction Reaction (ORR) process as it only requires a good dispersion of the N-CNTs in an ink medium before processing to make the electrode [11, 12] whereas for the other applications, involving gas—solid or liquid—solid reactions, the N-CNTs should be shaped in a macroscopic form in order to avoid the problem of pressure drop across the catalyst bed and also to facilitate the problem of reactor charging and discharging as well as the catalyst recovery. Chizari et al. [3] reported that N-CNTs supported on silicon carbide foam displays a significant

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http://dx.doi.org/10.1016/j.crci.2015.09.022

improvement in the desulfurization performance compared to the bulky N-CNTs. The main advantages of the macroscopic shaping using a SiC as a host structure not only reduce the problem of pressure drop but also allow one to control the problem of heat and mass transfer during the reaction by adapting the macroscopic shape to the reaction conditions which significantly enhance the overall catalytic performance [13, 14]. In this aim several research projects have been conducted to develop N-CNT supported on different macroscopic host structures, i.e. Al_2O_3, SiO_2, carbon and SiC, for different catalytic processes. The supports should also be produced in a simple and scalable way in order to avoid the costly development of new infrastructure and to reduce as much as possible the time to market the process. However, supported N-CNTs imply the use of inert supports which reduce the intrinsic catalytic activity per unit weight of the catalyst and thus, it is of interest to develop a new synthesis method to shape the N-CNTs directly without a need for support in order to improve the intrinsic activity.

The aim of the present article deals with the synthesis of the self-sustained nitrogen-doped carbon nanotubes with a controlled macroscopic shaping for subsequent use as metal-free catalyst in a gas-phase reaction. It is worthy to note that such direct macroscopic shaping of N-CNTs as well as their use as metal-free catalysts has not been reported so far in the literature. The synthesis method is based on a coagulation process using alginate as a gelling agent, followed by a thermal step to make entangled carbon nanotubes with a homogeneous size and shape. The as-synthesized N-CNT beads will be evaluated as metal-free catalysts in the gas-phase partial oxidation of hydrogen sulfide into elemental sulfur. The catalytic performance will be compared with that obtained on the Fe_2O_3 supported on silicon carbide catalysts which is one of the most active desulfurization catalysts [15, 16].

2. Experimental

2.1. N-CNT characteristics

The N-CNTs were synthesized by the catalytic chemical vapor deposition (CCVD) process using Fe/Al_2O_3 as the growth catalyst and C_2H_6 and NH_3 as carbon and nitrogen sources [17]. The N-CNTs were recovered after a consecutive base and acid treatment to remove the growth catalyst. The as-synthesized composite was first treated with a soda solution (20 wt. %) at 110 °C in order to dissolve the alumina support of the growth catalyst. The sample was thoroughly washed with distilled water until a neutral pH was reached and further treated with a solution of aqua regia at 110 °C followed by a washing process until neutral pH. The resulting bulky N-CNT sample was allowed to dry at 110 °C for overnight.

TEM analysis shows the presence of high aspect ratio N-CNTs containing bamboo-like caps along the tube length (Fig. 1A and B) which is in good agreement with the literature results. [18] The as-synthesized N-CNTs also exhibit a clean surface and no trace of carbon nanoparticles was observed which indicates the high selectivity of the synthesis method. The STEM-EELS analysis evidences the presence of nitrogen and carbon homogeneously dispersed within the tube matrix (Fig. 1C). [18] The X-ray photoelectron spectroscopy (XPS) analysis indicates that the purified N-CNTs contain about 0.12 at % of residual iron. The residual iron in the purified N-CNTs may be attributed to iron localized within carbon nanotubes or encapsulated by graphene layers and thus, is not accessible to the acid during the acid treatment. Such residual iron is expected to be not accessible to the reactant during the catalytic process.

2.2. N-CNT bead synthesis

The N-CNT bead synthesis was carried out as follows: 2 g of purified N-CNTs were dispersed in 100 mL of distilled water through a tip sonicator for 30 min [19]. The N-CNT suspension was kept under vigorous stirring (750 rpm) and 1 wt. % of alginate (with respect to the weight of the water) was slowly added to the suspension. The solution was kept under stirring for an additional 30 min. A drop of the N-CNT-alginate suspension was added to an aqueous $CaCl_2$ solution (3 wt. %). As soon as the drop comes into contact with $CaCl_2$ solution, N-CNT beads with a diameter of about 5 mm were steadily formed. The as-synthesized N-CNT beads were left inside the $CaCl_2$ solution overnight in order to complete the chemical reaction. The beads were washed with distilled water to remove as much as possible the residual salt. The beads were then dried at room temperature for 12 h and dried at 70 °C for 14 h and then, the alginate in the composite was decomposed by heating up to 600 °C under helium flow for 2 h. After the calcinations, the CNT beads were treated in HCl solution (20 vol. %) at room temperature for 2 h in order to remove as much as possible the remaining sodium and calcium species from the material before the catalytic evaluation process.

2.3. Characterization techniques

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 charging effect during the analysis.

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 ultrasound 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 N-CNTs and the beads, 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.

Thermogravimetric analyses (TGA) were performed under air (25 mL min^{-1}) on an EXSTAR thermogravimetric analyzer (TG/DTA) Seiko 6200.

The XPS measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW ClassWA