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Bucky paper with improved mechanical stability made from vertically aligned carbon nanotubes for desulfurization process

Adrien Deneuve[a,*], Kun Wang[a], Izabela Janowska[a], Kambiz Chizari[a], David Edouard[a], Ovidiu Ersen[b], Marc-Jacques Ledoux[a], Cuong Pham-Huu[a,**]

[a] Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, CNRS-Université de Strasbourg (UDS) UMR 7515, 25, rue Becquerel, 67087 Strasbourg Cedex 08, France
[b] Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS-Université de Strasbourg (UDS) UMR 7504, 23, rue du Loess, 67037 Strasbourg Cedex 02, France

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ABSTRACT

Bucky paper (BP) made from vertically aligned carbon nanotubes exhibits a high mechanical strength and flexibility owing to the high aspect ratio of the carbon nanotubes. Such macroscopic material with nanoscopic properties was efficiently used as a catalyst support in the gas-phase desulfurization reaction. The Fe_2O_3 (3 wt.%) supported on BP exhibits superior stability and activity in H_2S oxidation to sulphur compared with other catalysts supported on activated charcoal and carbon felt. The high stability of the Fe_2O_3/BP catalyst was attributed to the presence of a strong active phase-support interaction which prevents the active phase sintering during operation.

1. Introduction

Catalysis is nowadays considered as the backbone of the industrial chemistry and its industry represent the widest economy spectrum with an important value [1]. The researches within the catalysis field have been carried out with taking into account the green chemistry and sustainable development approach. For this purpose, a macro-shape design of the catalytic materials with nanoscopic properties is deeply related to the integration of new environmentally friendly processes with the significant up-grading of existing chemical processes. Carbon nanotubes, a one-dimensional carbon material, have received an over increasing scientific interest during the last decades due to their exceptional physical and chemical properties [2]. Apart from the electronic field of application, recent works have pointed out the possible use of carbon nanotubes, either pure or doped, as catalyst support in several potential reactions [3–6]. The material combines a high external surface area and high accessibility, due to its high aspect ratio and nanoscopic dimension, which reduce considerably diffusion issues. The extensive use of these nanomaterials opens a new way for designing high performance heterogeneous catalysts with controlled surface properties and catalyst structure which give rise to chemical processes with lower environmental impact. In most cases, carbon nanotubes were directly used in a bulk form and no attempt for macroscopic shaping was made. However, a direct use of bulky carbon nanotubes induces several drawbacks such as hard and hazardous manipulation and transport, and also a high pressure drop across the catalyst bed, especially in the case of fixed-bed configuration. Therefore, it is of interest to develop a new type of carbon nanotubes structure with controlled macroscopic shape for their subsequent use as catalyst support in the field of heterogeneous catalysis.

Bucky paper (BP) made from carbon nanotubes is reported to be an interesting material composite in several domains of application [7,8]. The works dealing with the use of vertically aligned carbon nanotubes (VA-CNTs) as catalyst support have also been reported [9,10]. However, the use of BP as catalyst support is lacking despite the high advantages that this material offers when used as heterogeneous catalyst support. Amongst these advantages one can cite: (i) high external surface area without ink-bottled pores which significantly improves the reactant access and product escape, (ii) surface functionalization by chemical treatment which increases the active phase dispersion and prevents an excessive sintering process during operation, and (iii) a relatively high thermal conductivity which could prevent hot spot formation due to the exothermic character of the reaction. In addition, the inter-tubes porosity can be also finely tuned by controlling the filtration pressure or by modifying the carbon nanotubes concentration in the solution.

In the present work we report the use of extremely high aspect ratio vertically aligned carbon nanotubes (VA-CNTs), in a form of bucky paper (BP), as a new support for the iron-

* Corresponding author. Tel.: +33 3 68 85 26 45; fax: +33 3 68 85 26 74.
** Corresponding author. Tel.: +33 368 852 667; fax: +33 368 852 674.
E-mail addresses: adrien.deneuve@etu.unistra.fr, deneuveadri@yahoo.fr (A. Deneuve), cuong.lcmc@ecpm.u-strasbg.fr (C. Pham-Huu).

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based active phase in the selective catalytic oxidation of trace amounts of H_2S into elemental sulphur. Such catalytic desulfurization process is of interest in the global reduction of harmful gaseous products in the atmosphere in order to meet the ever stricter legislation requirements [11,12]. Indeed, due to its high toxicity, H_2S must be removed as much as possible before releasing the off-gas into the atmosphere. The general trend is to transform selectively the H_2S into elemental sulphur using the equilibrated Claus process: $2H_2S + SO_2 \leftrightarrow (3/n)S_n + 2H_2O$ [13,14]. However, due to the thermodynamic equilibrium limitations of the Claus reaction, the maximum conversion is levelled at about 97% and thus, other process should be applied to remove the remaining 3%. The catalytic selective oxidation process is developed with the aim to perform complete removal of the remaining H_2S inside the Claus tail-gas using oxygen as oxidant [15,16]. Details concerning the selective oxidation process are summarised in several reviews devoted to this field, however, the catalyst which is the core of the process, still needs to be improved [17,18]. The catalytic performance of the BP supported iron catalyst is also compared with those obtained on more traditional supports namely activated charcoal and carbon felt. All the tested supports are thermal conductors which allows one to phase-out the problem of sulphur selectivity loss due to the local hot spot formation [19].

2. Experimental

2.1. Vertically aligned carbon nanotubes (VA-CNTs) synthesis, and catalyst supports

The VA-CNTs were synthesised by chemical vapor deposition, passing a mixture of $Fe(C_5H_5)_2/C_7H_{10}$ over a quartz substrate at 850 °C [10,20,21]. The quartz tubular reactor (length, 1100 mm, diameter, 50 mm) was housed inside an electric oven maintained at 850 °C. The liquid mixture consisting of ferrocene dissolved in a toluene medium (20 g/L) was injected with flowing argon (2 L/min) into the hot zone of the reactor thanks to a spray gun. The synthesis lasted for 2 h in order to obtain VA-CNTs with a length approaching ca. 2 mm. After the synthesis the substrate with VA-CNTs was cooled down under argon flow to room temperature before discharging from the reactor. The VA-CNTs were removed from the quartz substrate by treatment with HNO_3 at 120 °C for 6 h, which allowed a simultaneous removal of the residual iron catalyst from the nanotubes surface. The purified CNTs were next submitted to dispersion in ultrasonication bath for 2 h in an ethanol medium. The high aspect ratio of the VA-CNTs allows them to remain stable as an ethanol suspension for a long period, i.e. 24 h. The BP was made by filtration of the VA-CNTs suspension on Büchner filter device under pressure followed by drying at 170 °C overnight. Thus the final disk shape of the BP is obtained thanks to the Büchner shape.

Activated charcoal (AC) was purchased from Calgon Carbon Corporation in an extrudates form Xtrusorb 700 (length = 5 mm, diameter = 4 mm). This carbonaceous support exhibits both microporous and macroporous characters with an overall specific surface area of 880 m^2/g.

Carbon felt was purchased from Carbon Lorraine. It consists in a non porous matter having a relatively low specific surface area at around 1 m^2/g, which is constituted by an entangled network of carbon microfilaments with a few centimetres length and around ten micrometres of diameter.

The activated charcoal and carbon felt support have been treated in acid solution similarly to the vertically aligned carbon nanotubes in order to get the same surface feature.

2.2. Fe_2O_3-based catalyst preparation

The iron-based active phase was deposited onto different supports, i.e. BP, carbon felt and AC via incipient wetness impregnation using an iron nitrate salt as an active phase precursor. In order to increase the wetting of the support surface a mixture of water and ethanol (50:50 vol.%) of the salt was used. The iron loading was set at 3 wt.%. The solid was allowed to dry at 100 °C for 8 h and then calcined in flowing air for 2 h at 350 °C to transform the salt precursor into its corresponding oxide.

2.3. Characterisation techniques

The specific surface area of the different samples was measured by the BET method using N_2 adsorption–desorption isotherms at liquid nitrogen temperature (TriStar sorptometer). Before the measurement, the sample was out-gassed at 200 °C overnight in order to desorb moisture and impurities from its surface.

The XPS measurements on the supports surface were performed on a MULTILAB 2000 (THERMO) spectrometer equipped with Al Kα anode ($h\nu$ = 1486.6 eV) with 10 minutes of acquisition. A peak deconvolution has been made with "Avantage" program from Thermoelectron Company. The C_{1s} peak at 284.2 eV was used to correct the charging effects. The Shirley backgrounds were subtracted from the raw data to obtain the areas of the C_{1s} and O_{2p} peaks.

The growth morphology of the carbon nanotubes material was observed by scanning electron microscopy (SEM) on a Jeol F-6700 FEG. The sample was covered by a thin layer of gold in order to decrease the problem of charge during the analysis. Additionally, transmission electron microscopy (TEM) observation was conducted on a Topcon 002-B UHR microscope working at 200 kV accelerating voltage with a point-to-point resolution of 0.17 nm. The sample was roughly sonicated in an ethanol solution and a drop of the solution was deposited onto a copper grid covered with a holey carbon membrane for observation.

Zeta potential measurements and pH titration were carried out on the Nano-Zeta Sizer (multipurpose titrator, Malvern Instruments). The samples were sonicated in aqueous $NaClO_4$ electrolyte solution for 30 min before measurements. The titrations of the CNTs suspensions were performed using 10^{-1} M NaOH and HCl aqueous solutions. The Zeta potential values were determined from the particle velocities according to the Helmholtz–Smoluchowski equation: $\zeta = 4\pi\mu\eta/D$ where μ is the electrophoretic mobility, η is the viscosity, and D the dielectric constant of the liquid in the boundary layer.

2.4. Catalytic selective oxidation of H_2S into elemental sulphur

The selective oxidation of H_2S was carried out in a fixed-bed reactor at atmospheric pressure. An amount of "*x*" g (BP: 0.45 g; AC: 1.7 g; Felt: 0.55 g) and "*y*" ml (BP: 2.7 mL; AC: 2.8 mL; Felt: 5.0 mL) of catalyst was placed on a silica wool in a tubular Pyrex reactor (25.4 mm inner diameter and 600 mm height) housed inside a vertical tubular electrical furnace and the temperature was controlled by a K-type thermocouple and a Minicor regulator. The gas mixture was passed downward through the catalyst bed. The gases (H_2S, O_2, He) flow rate was monitored by Brooks 5850TR mass flow controllers linked to a control unit. The composition of the reactant feed was H_2S (1 vol.%), O_2 (2.5 vol.%), H_2O (30 vol.%) and He (balance). The relatively high concentration of steam in the feed was used in order to obtain the conditions as close as possible to the industrial working conditions. The steam formed during the former Claus units is not removed before the oxidation step and remains in the treated tail gas. Steam (30 vol.%) was fed to the gas mixture by bubbling the helium flow through a glass tank containing water at 70 °C. The molecular ratio between O_2 and H_2S was set at 2.5,