Contents lists available at ScienceDirect

Applied Catalysis A: General

Nitrogen-doped carbon nanotubes decorated silicon carbide as a metal-free catalyst for partial oxidation of H_2S

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ARTICLE INFO

ABSTRACT

Hierarchical metal-free catalyst based on the CVD synthesis of nitrogen-doped carbon nanotubes decorated silicon carbide (N-CNTs/SiC) macroscopic host structure has been prepared. The catalyst was evaluated in the partial oxidation of H_2S by oxygen into elemental sulfur in a fixed-bed reactor. The catalytic results indicate that the N-CNTs/SiC catalyst exhibits an extremely high desulfurization performance even under severe reaction conditions such as low temperature, high space velocity and at low O_2-to-H_2S molar ratio. The high desulfurization performance was attributed to the high effective surface area of the catalyst along with a short diffusion length associated with the nanoscopic dimension of the carbon nanotubes. The N-CNTs/SiC catalyst also displays a high stability as a function of time on stream which could be attributed to the strong anchoring of the nitrogen doping within the carbon matrix. The extrudates shape of the SiC support allows the direct macroscopic shaping of the catalyst for use in conventional fixed-bed reactor without facing problems linked with catalyst handling, transportation and pressure drop across the catalyst bed as encountered with nanoscopic carbon-based catalyst.

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1. Introduction

The last decade has faced an over increasing research on the development of metal-free catalysts for several catalytic applications such as oxygen reduction reaction (ORR) [1–3], selective steam-free dehydrogenation and oxidative dehydrogenation [4–7], transesterification [8,9], and selective oxidation [10–12]. Nitrogen-doped carbon nanotubes (N-CNTs) were the most studied metal-free catalysts [13–15] due to the very similar size between the nitrogen atom and carbon atom which allows an easy insertion of nitrogen atoms inside the carbon matrix [16]. It is also worthy to note that the metal-free catalysts display a higher activity and stability compared to their counterpart metal and/or metal oxide catalysts. In a recent review, Su et al. [17] have highlighted the advantages of using carbon-based metal-free catalysts for several catalytic reactions with an advantage on the active-site control. Dai et al. [3] have recently reviewed on the development and use of N-CNT and graphene metal-free catalysts, for the selective

dehydrogenation and oxidative dehydrogenation of alkanes and the ORR, which display better activity and stability compared to the metal-based catalysts. Bitter et al. [18] have also reported the high activity of the N-CNT in the Knoevenagel reaction. Recently, Peng et al. [12] have reported that N-CNT can be efficiently employed as metal-free catalyst in the selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. The N-CNT catalyst also exhibits an extremely high stability as a function of the cycling tests which could be attributed to the strong incorporation of nitrogen atoms in the carbon host matrix. Similar results have also been reported by Faba et al. [19] in the biomass upgrading processes: acetone aldol and acetic acid decarboxylative condensations. Recently, Su et al. [20] have also reported that sp^2 N-doped graphitic catalysts generate reactive oxygen species which allow one to perform the hydrocarbon activation even at room temperature. The high advantage of using these N-CNT catalysts versus the traditional metal/metal oxide supported ones is belong to the fact that the nitrogen species are well anchored within the catalyst structure and thus, problems linked with the active phase sintering are unlikely to occur.

The international restrictions concerning the release of sulfur compounds containing gas into the atmosphere are becoming more

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and more drastic during the last decades [21]. Nowadays, a large amount of hydrogen sulfide (H_2S) is released from crude oil, natural gas refineries and metal smelting process in steel production. It is also worthy to note that the coal liquefaction process is also considered to be the major source of H_2S emission in the near future [22]. A large part of the H_2S was removed via the Claus process [23] while the residual un-reacted H_2S will be converted into elemental sulfur at different reaction temperatures through the Super-Claus process [24,25]. In a recent study we have reported that N-CNT and N-CNTs/SiC foam are efficient metal-free catalysts for performing the high temperature selective oxidation of H_2S into elemental sulfur at a relatively high space velocity [11]. In addition, owing to the well anchorage of the nitrogen species inside the carbon matrix no deactivation was observed for a long-term reaction which was not the case with traditional supported catalyst where deactivation by sintering could occur. The problem linked with the transport/handling and pressure drop across the catalyst bed, belonging to the nanoscopic structure of the N-CNT, can be avoided by supporting them on a macroscopic host structure of silicon carbide (SiC) [11]. However, the high porous volume of the SiC foam support (>90%) presents a drawback for industrial application due to its relatively low active phase loading per unit volume of the reactor. It is of interest to optimize the synthesis process of the hybrid composite and to develop new support with a higher density in order to fulfill the industrial requirements.

The aim of the present study is to report on the high desulfurization performance of the metal-free nitrogen-doped carbon nanotubes (N-CNTs) immobilized on a silicon carbide (SiC) extrudates host structure with high density. It is expected that the macroscopic shaping of the catalyst allows the avoidance of problems linked with handling and pressure drop for applications in a fixed-bed reactor. This hybrid catalyst exhibits an extremely high desulfurization performance along with a low pressure drop even at high reactant weight hourly space velocity (WHSV). The results highlighted the strong influence of the N-CNTs loading on the desulfurization performance which has ever been reported before. The desulfurization performance was also bench-marked with those obtained on the Fe_2O_3/SiC which is one of the most active and selective catalyst for the selective oxidation of H_2S into elemental sulfur [26,27].

2. Experimental

2.1. Silicon carbide supports

Silicon carbide (β-SiC) in an extrudates shape was synthesized via a gas–solid reaction between SiO vapor and dispersed solid carbon. The detailed synthesis of the SiC-based materials is summarized in a recent review [28]. The β-SiC was synthesized by mixing microsized silicon powder with a carbon-containing resin. The paste will be further shaped into desired shape, i.e. extrudates, grains, beads, etc. Examples of the medium to high surface area SiC with different size and shape synthesized by an industrial gas–solid process are presented in Fig. 1. The carburization process was carried out under flowing argon at temperature around 1350 °C during 1 h. The as-synthesized SiC was further calcined in air at 700 °C for 2 h in order to remove the un-reacted carbon within its matrix. The resulted SiC material was thus partly covered with a thin layer of SiO_2 and SiO_xC_y (Fig. 1B) which could play the role of anchorage site for dispersing metal nanoparticles on its surface [29,30].

2.2. Synthesis of the N-CNT/SiC composite

The N-CNT/SiC composite was synthesized according to the Chemical Vapor Deposition (CVD) method with iron as a growth

catalyst [31,32]. The Fe/SiC (7 wt.%) catalyst was synthesized by impregnating the SiC support with an aqueous solution containing $Fe(NO_3)_3$. The solid was dried at room temperature overnight and oven-dried at 110 °C for 24 h. It was then calcined in air at 350 °C for 2 h in order to transform the nitrate precursor into its corresponding oxide. The Fe_2O_3/SiC catalyst was housed in a quartz reactor localized inside an electric furnace. The catalyst was reduced under hydrogen flow (200 mL/min) at 400 °C for 2 h and then, the reaction temperature was raised to the synthesis temperature (heating rate of 10 °C min^{-1}) and the H_2 flow was replaced by a C_2H_6/NH_3/H_2 mixture. The XRD patterns of the iron-based growth catalyst after calcination and reduction (not shown) confirm the complete reduction of the Fe_2O_3 phase. The C_2H_6, NH_3, and H_2 flow rates, used in the synthesis of N-CNT/SiC, were fixed at 50:50:20 sccm min^{-1}. The synthesis was lasted for 2 h, and the reactor was cooled to room temperature under argon. For the unsupported N-CNTs the Fe/Al_2O_3 growth catalyst was used instead of Fe/SiC and the similar process was used.

For the unsupported N-CNTs, growth from the Fe/Al_2O_3 catalyst, the as-synthesized product was treated by a NaOH (20 wt.%) solution at 80 °C for 24 h followed by an acid treatment (HNO_3, 32 vol.% at 80 °C) for 24 h in order to remove both the support and the growth catalyst. The solid was washed thoroughly with distilled water between the treatment processes. Elemental analysis performed on the treated N-CNTs indicates that about 0.2 wt.% of residual iron remains in the catalyst. Such residual iron could be attributed to the iron encapsulated within the carbon nanotubes which was not being accessible to the acid during the purification process. For the supported N-CNTs/SiC sample the solid was only treated with an acid solution under the same conditions. The washed catalyst contains a residual iron of about 0.4 wt.% according to the elemental analysis. TEM-EELS analysis on both samples indicates that the nitrogen concentration was higher in the arches region while lower nitrogen concentration was observed on the tube wall [33] and confirms the similar growth mode on both unsupported and supported materials.

2.3. Characterization techniques

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 grinded and then dispersed by ultrasounds in an ethanol solution for 5 min and a drop of the solution was deposited on a copper grid covered with a holey carbon membrane for observation.

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 thermal gravimetric analysis (TGA) was carried out on a TA Instruments Model Q-5000. The known amount of sample (10 mg) was loaded into a platinum crucible and heated up in air from room temperature to 1000 °C with a heating rate of 5 °C min^{-1}.

The specific surface area of the support and the catalyst, after reduction, 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 measurements were carried out using N_2 as adsorbent at liquid N_2 temperature at relative pressures between 0.06 and 0.2.

The X-ray photoelectron spectroscopy (XPS) measurements of the support and catalyst were performed by using a MULTILAB 2000 (THERMO) spectrometer equipped with an Al Kα anode ($h\nu$ = 1486.6 eV) with 10 min of acquisition to achieve a good signal to noise ratio. Peak deconvolution was performed with the "Avantage" program from the Thermoelectron Company. The C1s