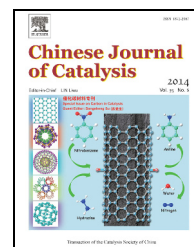


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Nitrogen-doped carbon nanotubes on silicon carbide as a metal-free catalyst

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ABSTRACT

A hierarchical metal-free catalyst consisting of nitrogen-doped carbon nanotubes decorated onto a silicon carbide (N-CNTs/SiC) macroscopic host structure was prepared. The influence of N-CNTs incorporation on the physical properties of the support was evaluated using different characterization techniques. The catalyst was tested as a metal-free catalyst in the selective oxidation of H₂S and steam-free dehydrogenation of ethylbenzene. The N-CNTs/SiC catalyst exhibited extremely good desulfurization performance compared to a Fe₂O₃/SiC catalyst under less conducive reaction conditions such as low temperature, high space velocity, and a low O₂-to-H₂S molar ratio. For the dehydrogenation of ethylbenzene, a higher dehydrogenation activity was obtained with the N-CNTs/SiC catalyst compared to a commercial K-Fe/Al₂O₃ catalyst. The N-CNTs/SiC catalyst also displayed good stability as a function of time on stream for both reactions, which was attributed to the strong anchoring of the nitrogen dopant in the carbon matrix. The extrudate shape of the SiC support allowed the direct macroscopic shaping of the catalyst for use in a conventional fixed-bed reactor without the problems of catalyst handling, transportation, and pressure drop across the catalyst bed that are encountered with nanoscopic carbon-based catalysts.

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1. Introduction

The last decade has seen 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]. The very similar size between the nitrogen atom and carbon atom allows an easy insertion of nitrogen atoms inside the carbon matrix [16]. It is

also noteworthy that the metal-free catalysts often displayed higher activity and stability than metal and/or metal oxide catalysts. In a recent review, Su et al. [17] and Dai and co-workers [3] highlighted the advantages of using carbon-based metal-free catalysts for several catalytic reactions with an important advantage being the active site control. Recently, Peng and co-workers [18] reported that N-CNTs could be efficiently employed as a metal-free catalyst in the selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. The N-CNTs catalyst also exhibited extremely high stability in the recycling tests. Recently, Su and co-workers [19] also reported

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that sp^2 N-doped graphitic catalysts generated reactive oxygen species which allowed one to perform hydrocarbon activation even at room temperature. The big advantage of using these N-CNTs catalysts versus the traditional metal/metal oxide supported ones is due to that the nitrogen species are well anchored within the catalyst structure and thus, problems linked with active phase sintering are unlikely to occur even under severe reaction conditions.

The aim of the present article is to report on the use of metal-free nitrogen-doped carbon nanotubes (N-CNTs) immobilized on a silicon carbide (SiC) extrudate host structure for catalytic applications. The macroscopic shaping of the catalyst allowed the avoidance of the problems of handling and pressure drop for applications in a fixed bed reactor [20]. The two probe reactions used in the present work to evaluate the catalytic activity of the N-CNTs/SiC catalyst were the selective oxidation of H_2S into elemental sulfur and the steam-free dehydrogenation of ethylbenzene into styrene. The influence of the reaction conditions on the catalytic performance was thoroughly investigated and the results were discussed using the characterization data. The stability of the catalysts was also evaluated in a long-term process.

2. Experimental

2.1. Silicon carbide supports

Silicon carbide (β -SiC) in an extrudate shape was synthesized by a gas-solid reaction between SiO vapour and dispersed solid carbon. The detailed synthesis of the SiC-based materials was summarized in a recent review [21]. The β -SiC was synthesized by mixing microsized silicon powder with a carbon-containing resin. The paste was further shaped into the desired shape, i.e. extrudates, grains, beads, etc., before carburization. The carburization process was carried out under flowing argon at a temperature around 1350 °C for 1 h. 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(a). The as-synthesized SiC was further calcined in air at 800 °C for 2 h to remove residual carbon. The resulting SiC material was thus partly covered with a thin layer of SiO_2 and SiO_xC_y (Fig. 1(b)), which could play the role of anchorage site for dispersing metal nanoparticles on its surface [22–24].

2.2. Synthesis of the N-CNTs and N-CNTs/SiC composite

The N-CNTs and N-CNTs/SiC composite (nitrogen-doped carbon nanotube decorated β -SiC extrudate) were synthesized by the chemical vapor deposition (CVD) method [25,26]. The synthesis of the N-CNTs/SiC composite was as follows. First, an aqueous solution containing $Fe(NO_3)_3$ (7 wt% Fe) was introduced onto the surface of SiC extrudates by incipient wetness impregnation. The Fe/SiC sample 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 to transform the nitrate precursor into the corresponding oxide. The Fe_2O_3 /SiC catalyst was placed in a quartz reactor that was then put inside an elec-

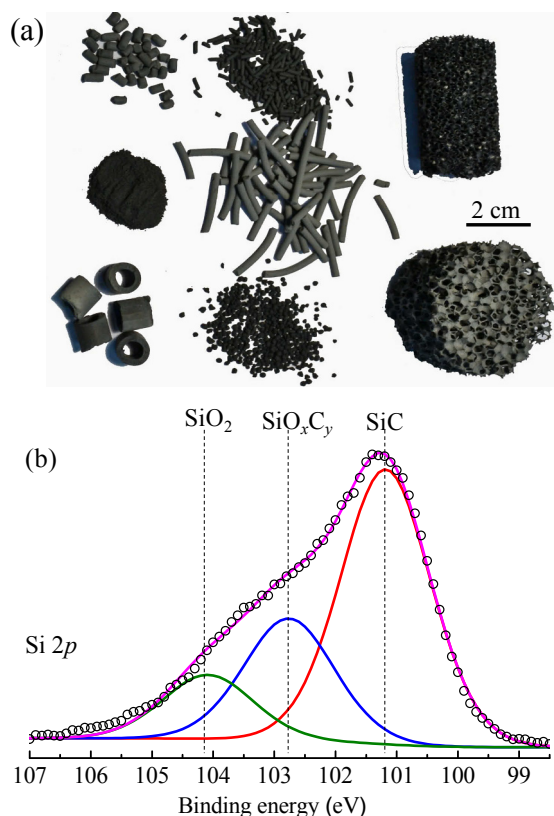


Fig. 1. (a) Macroscopic shapes, i.e., grains, extrudates, foams, and rings of silicon carbide synthesized by a gas-solid reaction (www.sicatcatalyst.com). (b) XPS Si 2p of the SiC surface showing the presence of SiC, SiO_xC_y , and SiO_2 .

tric furnace. The catalyst was reduced under H_2 flow (200 mL/min) at 400 °C for 2 h and then, the temperature was raised to 750 °C (heating rate of 10 °C/min) and the H_2 flow was replaced by a $C_2H_6/NH_3/H_2$ mixture. The X-ray diffraction (XRD) patterns of the Fe-based catalyst after calcination and reduction (not shown) confirmed the complete reduction of the Fe_2O_3 phase before the CNT-growth process. The C_2H_6 , NH_3 , and H_2 flow rates were 50, 50, and 20 mL/min, respectively. The synthesis was continued for 2 h, and the reactor was cooled to room temperature under argon. Unsupported N-CNTs were synthesized by a commercial Fe/Al_2O_3 catalyst instead of Fe/SiC . A similar process was used.

The N-CNTs-based composite was chemically treated before catalytic evaluation as described below. For the N-CNTs/SiC sample, the material was only treated with an acid solution (HNO_3 , 65 vol%) at 80 °C for 12 h in order to remove the CNT-growth catalyst. Transmission electron microscopy-electron energy loss spectroscopy (TEM-EELS) analysis of both samples indicated that the nitrogen concentration was higher in the arch region while a lower nitrogen concentration was observed on the tube wall [27], which confirmed a similar growth mode on both the unsupported and supported materials. For the N-CNTs grown from the Fe/Al_2O_3 catalyst, the synthesized product was treated by a NaOH (20 wt%) solution at 80 °C for 24 h followed by an acid treatment (HNO_3 , 65 vol%) at 80 °C for 12 h in order to remove the support and CNT-growth cata-

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