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Few-layer sp^2 carbon supported on Al_2O_3 as hybrid structure for ethylbenzene oxidative dehydrogenation

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ABSTRACT

Hybrid materials consisting of few-layer sp^2 carbon supported on Al_2O_3 can potentially display comparable performance with nanodiamonds for the oxidative dehydrogenation of ethylbenzene. The hybrid structure could be easily prepared by fast coking method using ethanol as a precursor and γ-Al_2O_3 with high specific surface areas as a template. In this case, γ-Al_2O_3 plays the role of 3D support for depositing few-layer graphene-like structure. The hybrid structure exhibiting similar structure with nanodiamonds calcined at high temperature is further used as a metal-free catalyst for the oxidative dehydrogenation of ethylbenzene to styrene. The yield rate of styrene normalized by the specific area on Al_2O_3@C is 0.044 mmol m^{-2} h^{-1} (TOF = 4.13 h^{-1}) which is two times of that on nanodiamonds (0.020 mmol m^{-2} h^{-1}, TOF = 3.27 h^{-1}). Considering the low cost process and good catalytic performance, the hybrid nanostructure may be a promising candidate to be applied in the oxidative dehydrogenation of ethylbenzene.

1. Introduction

Carbon-based catalyst has attracted great interest in the past decades due to its unique properties for the direct dehydrogenation (DDH) and oxidative dehydrogenation (ODH) of hydrocarbons [1,2]. Among many kinds of nanocarbons (e.g. carbon nanofibers, mesoporous carbon), it is found that nanodiamonds (NDs) and onion-like carbons (OLCs) display a high catalytic activity in DDH/ODH of ethylbenzene (EB) to styrene (ST) [3–5]. The high activity of the NDs may be attributed to the presence of a unique sp^2-sp^3 carbon hybrid structure, which provides a partial delocalization of the electron density [6]. Presently, most of the commercially available NDs in powder form are produced by an explosion method followed by nitric/sulfuric acid purification, resulting in high price of NDs and a mass of waste acid [7]. Moreover, the surface of fresh NDs usually contains amorphous carbon [8]. In order to obtain sp^2-sp^3 hybrid NDs, it is necessary to treat NDs at high temperature, generally above 1100 °C [9]. Therefore, it is imperative to further explore available and low-cost alternatives with comparable catalytic performance.

Recently, the template (e.g. metal oxides) method have attracted considerable attention because the structure of as-prepared carbon materials could be controlled by tuning the size or morphology of the template [10,11]. After the removal of template (generally, acid treatment method), hollow carbon nanostructures with amorphous or graphitic structure will be obtained, which has attracted considerable attention owing to their potential applications in catalyst supports, and lithium-ion batteries [12–14]. For the template method, the core-shell structure is synthesized by coating a carbon precursor on a hard template core, followed by carbonization or directly by CVD method. It is available to obtain a hybrid structure consisting of few-layer sp^2 carbon supported on a hard template core by regulating the synthesis conditions, such as temperature, the amount and type of precursor.

Here in this paper, we report a facile and large-scale method to synthesize hybrid nanostructure consisting of γ-Al_2O_3 core wrapped with 2–5 layer graphitized carbon (Al_2O_3@C) by a CVD process at 800 °C using commercial γ-Al_2O_3 powder as a template. The as-prepared hybrid nanostructure is used as a catalyst for the ODH of EB and exhibits a comparable activity with NDs. The yield rate of styrene normalized by the specific area on Al_2O_3@C is 0.044 mmol m^{-2} h^{-1} (TOF = 4.13 h^{-1}) which is two times of that on NDs (0.020 mmol m^{-2} h^{-1}, TOF = 3.27 h^{-1}). Considering the low cost process and good catalytic performance, the hybrid nanostruc-

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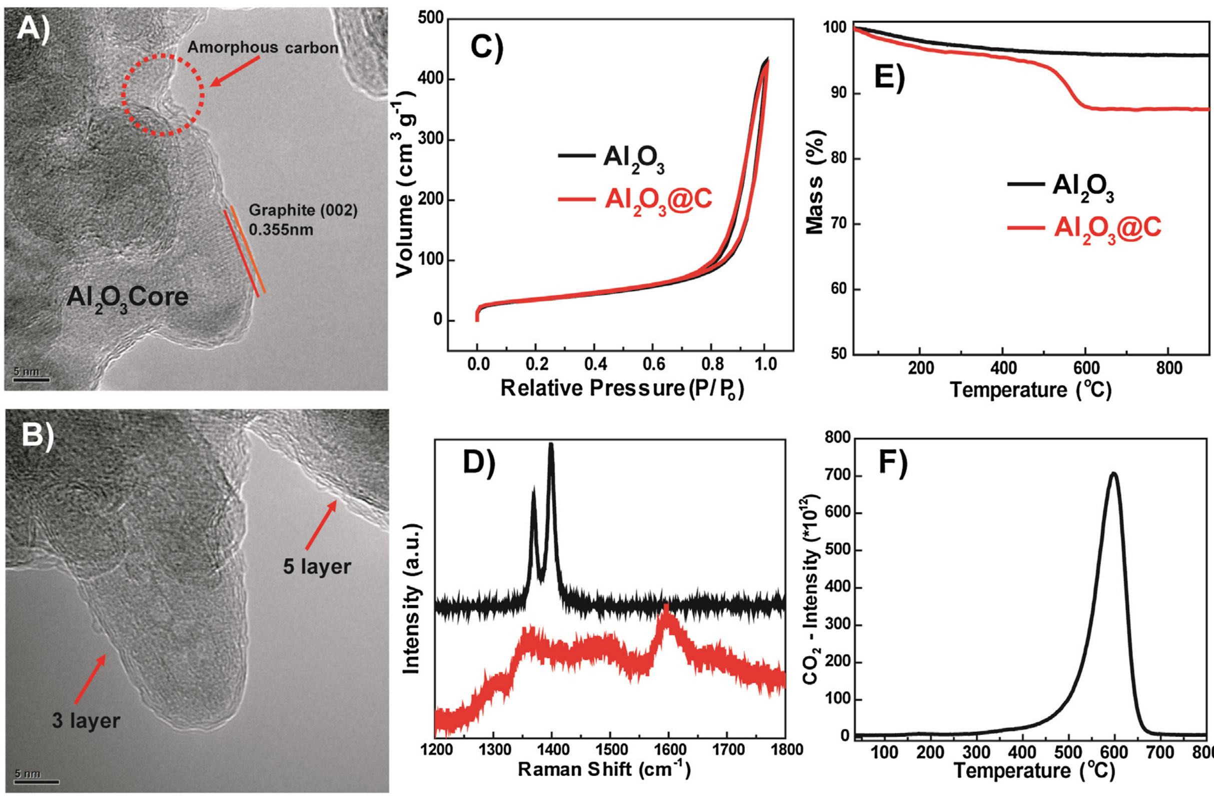

Fig. 1. A) and B) Typical HR-TEM images of fresh Al_2O_3@C. C) N_2 adsorption-desorption curves of γ-Al_2O_3 (black line) and Al_2O_3@C (red line). D) Raman spetra of γ-Al_2O_3 (black line) and Al_2O_3@C (red line). E) TG curves of γ-Al_2O_3 (black line) and Al_2O_3@C (red line). F) The off gas (CO_2: 44) monitored by an online mass spectroscopy of Al_2O_3@C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ture will be a promising candidate to be applied in the ODH of EB.

2. Experimental

2.1. Catalyst preparation

γ-Al_2O_3 powder was purchased from Sinopharm Chemical Reagent Corp. Hybrid nanostructure (Al_2O_3@C) was synthesized by a CVD process at 800 °C using ethanol as a precursor and γ-Al_2O_3 powder as a template. NDs with different content of sp^2 carbon on the surface was obtained by calcining NDs at 900 °C, 1100 °C and 1300 °C in Ar atmosphere, respectively.

2.2. Catalyst characterization

Nitrogen adsorption-desorption data were measured with a Micromeritics ASAP 2020 analyser at 77 K. Prior to the measurements, the samples were degassed at 120 °C for 12 h. The specific surface area were calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.02 to 0.20. The total pore volumes (V_t) were estimated on the basis of the adsorbed amount at a relative pressure of 0.985. Raman spectra tests of samples on SiO_2/Si were performed with a Labram HR800 spectrometer and a He/Ne laser at 633 nm (50 × objective) was selected as the excitation source. The oxidation stability tests were carried out by a thermogravimetric analyzer (Netzsch 449 F3) connected with an online mass spectroscopy to monitor the off gas (CO_2: 44). About 5 mg of the sample was placed in a corundum crucible. The samples were heated from 35 to 900 °C at a rate of 20 °C min^{-1} under a gas flow of 50 ml min^{-1} comprising 10 vol% O_2 in Ar. Transmission election microscopy (TEM) images were characterized by a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV.

2.3. Catalytic reaction

The ODH of EB to ST reaction was carried out in a fix-bed quartz reactor at 450 °C and at atmospheric pressure. 50 mg of catalyst was fixed between two quartz wool plugs in the isothermal zone. The reactant flow was a mixture of 2.8 vol% EB and oxygen (O_2/EB ratio of 1:5) diluted in helium; the total space velocity was 12000 $cm^3\ g^{-1}\ h^{-1}$. No steam was added to the reactor. The reactants and products were analyzed by an online gas chromatography (Agilent 7890) using a HP-5 capillary column connected to FID and a CarboPlot capillary column connected to TCD. EB conversion of blank experiment was only 0.12% which can be ignored.

3. Results and discussion

NDs consisting of sp^3 core and sp^2 shell is obtained at high temperature (<1300 °C) under inert atmosphere. The layer amount of sp^2 carbon increases with the calcination temperature and onion-like carbons (OLCs) could be obtained by treat NDs when temperature is above 1300 °C [9,15]. However, the harsh synthesis conditions (e.g. high temperature) limits their large-scale industrial application. Typical HR-TEM images of Al_2O_3@C hybrid structure are shown in Fig. 1A and B. A clear Al_2O_3 nanocore wrapped with few-layer (2–5 layers) graphene-like carbon is observed. The N_2 adsorption-desorption curve of Al_2O_3@C is almost coincident with that of Al_2O_3 (Fig. 1C), suggesting that the deposition process of carbon is along with the outer surface of Al_2O_3, which is consistent with the result of HR-TEM. Table 1 summarizes the textural characterization of the samples. The specific surface area of Al_2O_3@C is