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Preparation and evaluation of molybdenum modified Fe/MgO catalysts for the production of single-walled carbon nanotubes and hydrogen-rich gas by ethanol decomposition

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ABSTRACT

Catalytic decomposition of ethanol over a molybdenum modified Fe/MgO catalyst to synthesize carbon nanotubes and hydrogen-rich gas is evaluated at temperatures between 600 and 900 °C. The results show that molybdenum modified Fe/MgO is an effective catalyst for the production of single-walled carbon nanotubes and hydrogen at 800 °C. According to the gaseous and solid products obtained, the reaction pathways for ethanol decomposition are suggested. Catalytic activities and stabilities of Fe/MgO and molybdenum modified Fe/MgO catalysts on ethanol decomposition are compared. The results show that the catalytic performance for the production of carbon nanotubes and hydrogen from ethanol decomposition can be improved significantly after the modification of molybdenum.

Introduction

Carbon nanotubes (CNTs) have been regarded as attractive building blocks for future nanoscale electronic devices, such as molecular sensors, field-emitting devices and field-effect transistors due to their unique electrical, mechanical, electro-optical and electromechanical properties [1–3]. There are currently three common methods for the production of the material: arc discharge, laser vaporization, and chemical vapor deposition (CVD) [4–6]. Among these methods, CVD has attracted great attention because of its potential use for industrial scale production of high-quality CNTs at low cost. Up to now, a large number of carbon sources, such as methane, acetylene and ethanol have been utilized in CVD for CNT production [7–10]. Among the various sources that can be converted into CNTs, ethanol is a very promising candidate due to its low production costs, easy-generation from renewable resources and low toxicity. The successful production of CNTs over various catalysts by ethanol CVD has been reported by many research groups [11–16]. However, in these reported literatures, researchers were mainly focused their interest on the formation of CNTs with controlled size, diameter, or structure. The synthesis of gaseous product, such as hydrogen, accompanied by CNT formation was rarely mentioned and investigated in their research works.

Hydrogen is expected to become an important power source for sustainable energy consumption due to its high conversion efficiency and low pollutant emissions [17,18]. There are a number of emerging and attractive approaches or process for hydrogen production, such as the natural gas catalytic decomposition, steam reforming, photocatalytic decomposition of water and biomass gasification [19–23]. Besides the above traditional methods, catalytic decomposition of ethanol is another way to produce hydrogen. Up to now, the preparation and evaluation of various catalysts in the production of hydrogen from ethanol CVD have been reported by several research groups [24–27]. However, their results indicated that amorphous carbon was easily formed during the CVD process. The formation of such solid product cannot be used further and it always has negative effect on the performance of the catalysts. Economic analysis has shown that if the carbon produced in ethanol CVD process can be utilized, it will be financially attractive [28].

Considering the potential applications of CNTs, it is speculated that if CNTs can be produced accompanied by hydrogen production through the ethanol CVD process, the ethanol decomposition will become more valuable and attractive. Inspired by this, in the

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present work, a Fe-Mo/MgO catalyst was synthesized and its catalytic activity for the production of single-walled carbon nanotubes (SWCNTs) and hydrogen-rich gas from ethanol CVD was studied. The purpose of the work is to explore optimum experiment conditions to produce high-yield hydrogen and high-quality SWCNTs simultaneously, which may have important technological application both in the fields of energy and material science.

Experimental

Preparation of catalyst

The MgO support was prepared by the co-precipitation method, using $Mg(NO_3)_2$ and $NH_3{\cdot}H_2O$ as the starting materials. The detailed procedure was as follows: 12.8 g $Mg(NO_3)_2$ was dissolved in 200 ml deionized water, and then 25 ml $NH_3{\cdot}H_2O$ (25 wt.%) was added into the above solution gradually with constant stirring for 10 h to form a white colloid. The mixture was aged at room temperature for 24 h and then the formed colloid was washed by deionized water to remove $NH_3{\cdot}H_2O$, followed by drying at 80 °C for 12 h and calcined in air at 500 °C for 10 h.

The Fe-Mo/MgO catalyst system with stoichiometric composition of (Fe:Mo:MgO = 8.5:1.5:90 mol%) utilized in this study for SWCNT growth was prepared by impregnation method as follows: 1 g MgO powders were impregnated into 100 ml aqueous solution containing appropriate quantities of $Fe(NO_3)_3.9H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ with constant stirring for 12 h. Then the impregnated samples were dried at 80 °C until the excess water was evaporated, followed by calcination at 500 °C for 10 h. The final catalyst was obtained after the reduction of the calcined powders in presence of H_2 prior to the decomposition reaction. For comparison, Fe/MgO catalyst was also synthesized follow the same procedure except that no Mo was added. The amount of Fe in Fe/MgO was adjusted to 10 mol%.

Ethanol decomposition

The reaction apparatus used for ethanol decomposition was a conventional gas flow system with a vertical fixed bed at the center of a quartz tubular reactor (inner diameter 5 mm). The temperature of the bed was monitored with a thermocouple touched to the outside wall of the reactor in close proximity to the catalyst disk. Prior to ethanol decomposition, the catalyst (150 mg) was reduced by hydrogen at 900 °C for 1 h. After reduction, the decomposition of ethanol was performed on the catalysts at the temperature of 600–900 °C. Ethanol was injected through a microinjector into a vaporizing chamber (100 °C) at a flow rate of 0.3 ml h^{-1} and switched to the tubular reactor using Ar (40 ml min^{-1}) as the carrier gas. During ethanol decomposition, the gaseous products in the exit gas from the tubular reactor were analyzed at 12 min intervals by a gas chromatograph with a thermal conductivity detector and a flame ionization detector (GC/TCD-FID). After 60 min, the ethanol feed was stopped. The solid products were collected from the tubular reactor.

Characterization

The scanning electron micrograph (SEM) images of the solid products by ethanol decomposition were measured using a FEI Quanta 400 ESEM-FEG (environmental scanning electron microscope-field emission gun). The transmission electron microscope (TEM) images of CNTs were recorded with a JEOL JEM-3010 high-resolution transmission electron microscope (HRTEM) equipped with an X-ray energy dispersive spectrometer (EDS) at an

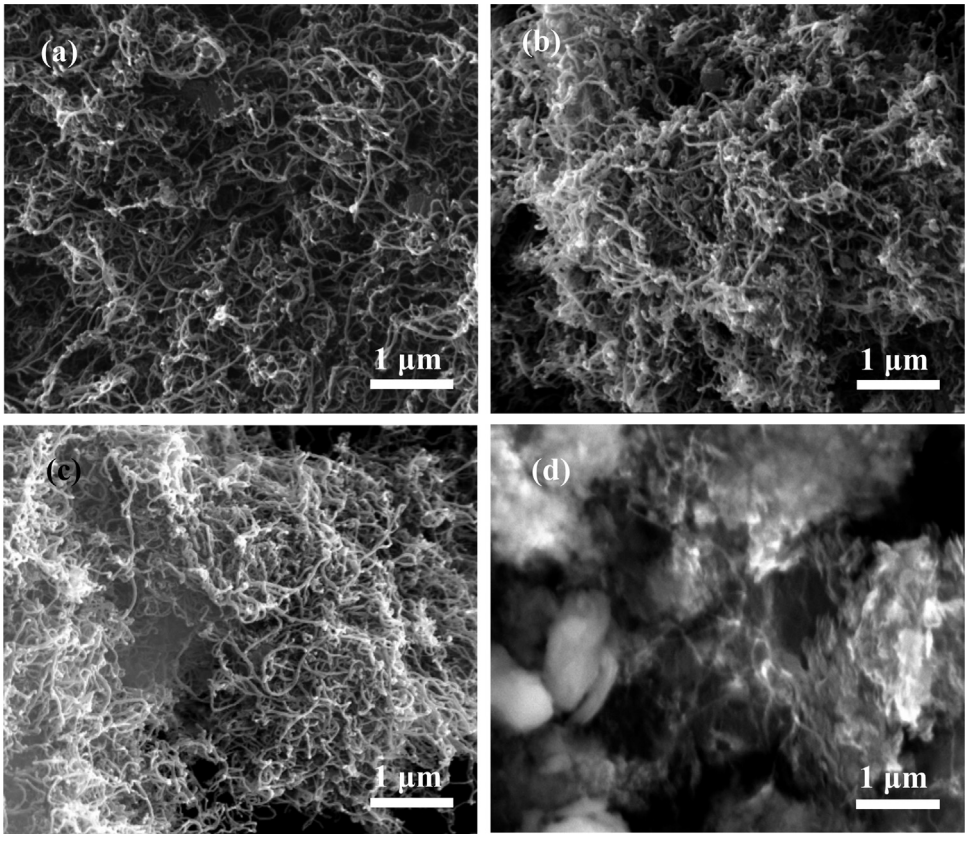

Fig. 1. SEM images of CNTs formed by ethanol decomposition over Fe-Mo/MgO catalyst at different temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.