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Production of hydrogen-rich gas and multi-walled carbon nanotubes from ethanol decomposition over molybdenum modified Ni/MgO catalysts

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Abstract

A series of molybdenum modified Ni/MgO catalysts (Ni-Mo/MgO) with different loading ratios of Ni : Mo were prepared by impregnation method. Ethanol decomposition to co-produce multi-walled carbon nanotubes and hydrogen-rich gas at temperatures of 600–800 °C was investigated over the synthesized Ni-Mo/MgO catalysts. The results showed that the catalytic activity depended strongly on the reaction temperature and loading ratio of Ni : Mo. According to the gaseous and solid products obtained, the reaction pathways for ethanol decomposition were suggested.

Key words

Ni-Mo/MgO; ethanol decomposition; hydrogen-rich gas; MWCNTs

1. Introduction

Carbon nanotubes (CNTs), a two-dimensional nanostructure of carbon materials, have attracted intense attention worldwide because of their excellent physical and chemical properties [1,2]. Currently, chemical vapor deposition (CVD) is known as a simple and convenient method for mass production of CNTs [3,4]. And a large number of carbon sources, such as methane, acetylene and ethanol have been utilized in CVD for CNT production [5−9]. Among the various fuels that can be converted into CNTs, ethanol is a pretty promising candidate owing to its low-toxicity, easy-generation from renewable resources, low production costs and relatively high hydrogen content [10−12]. It has been reported that single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs) were successfully synthesized by CVD using ethanol as carbon source over various catalysts [13−15]. However, in these reported literatures, researchers were mainly focused their interest on the formation of CNTs or CNFs with controlled size, diameter, or structure. The synthesis of gaseous product like hydrogen accompanied by CNT formation was rarely mentioned and investigated in their research works.

Hydrogen is being promisingly considered as a strategic fuel, due to its high conversion efficiency and low pollutant emissions [16]. It can be produced traditionally by water electrolysis, gasification reactions, partial oxidation reactions of heavy oil and hydrocarbon steam reforming reactions [17−22]. Except for the above hydrogen production methods, catalytic decomposition of ethanol is another way to produce hydrogen. Up to now, extensive studies have been carried out to prepare and evaluate various catalysts in the production of hydrogen from ethanol CVD [23−28]. However, their results indicated that amorphous carbon was easily formed during CVD process. The formation of such solid product can not be used further and it always has negative effect on the performance for hydrogen production. Economic analysis has shown that if the carbon produced in ethanol CVD process can be utilized, it will be financially attractive [29]. Considering the potential applications of CNTs, it is speculated that if CNTs can be produced accompanied by hydrogen production through ethanol CVD process, the decomposition of ethanol will become more valuable and attractive.

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Recently, Fe/Al_2O_3 catalyst was prepared by co-precipitation method in our group. The co-production of hydrogen and CNTs from ethanol decomposition over the catalyst at different temperatures and feeding rates of ethanol was investigated [30]. The results indicated that supported Fe metal catalyst was effective for hydrogen production and CNT growth. The positive catalytic performance of Fe for ethanol decomposition has been confirmed by us. However, it is still a challenge for us to produce high-quality CNTs accompanied by hydrogen production during the reaction. Molybdenum (Mo) modified Ni/MgO (Ni-Mo/MgO) is considered to be an effective catalyst for the decomposition of various hydrocarbon compounds to produce high-quality MWCNTs [31−37]. Although many researchers have investigated its catalytic performance on CNT growth, its activity on hydrogen production accompanied by carbonaceous formation was rarely studied. Considering the potential advantages of the catalyst, herein, a series of Ni-Mo/MgO with different loading ratios of Ni : Mo were synthesized and their catalytic activity for the co-production of hydrogen-rich gas and MWCNTs from ethanol CVD was investigated for the first time. The purpose of the work is to explore optimum experiment conditions to produce hydrogen-rich gas and high-quality MWCNTs simultaneously, which may have important technological application both in the fields of energy and material science.

2. Experimental

2.1. Catalyst preparation

All chemicals used in this study were analytic-grade reagents and used without further purification. MgO support was prepared by 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.

Ni-Mo/MgO catalysts were prepared by conventional impregnation method with total metals loading adjusted to 10 mol%. Three different Ni : Mo loading ratios of 1 : 1, 5 : 1 and 9 : 1 were prepared and defined as Ni1Mo1, Ni5Mo1 and Ni9Mo1, respectively. In a typical synthesis procedure, 1.0 g MgO powder was impregnated into 100 mL aqueous solution containing appropriate quantities of $Ni(NO_3)_2{\cdot}6H_2O$ 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 catalysts were obtained after the reduction of the calcined powder in the presence of H_2 prior to the decomposition reaction.

2.2. 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 touching the outside wall of the reactor in which the sample bed was located. Prior to ethanol decomposition, the catalyst (150 mg) was reduced by hydrogen at 500 °C for 1 h and subsequently purged under Ar at the same temperature for 40 min. The decomposition of ethanol was performed over Ni-Mo/MgO in the temperature range of 600–800 °C. Ethanol was injected through a microinjector into a vaporizing chamber (100 °C) at a flow rate of 0.3 mL/h and switched to the tubular reactor using Ar (40 mL/min) as the carrier gas. During ethanol decomposition, the gaseous products in the exit gases from the tubular reactor were analyzed at 12 min intervals by a gas chromatography with a thermal conductivity detector and a flame ionization detector (GC/TCD-FID). After 60 min, ethanol feed was stopped. The solid products were collected from the tubular reactor.

2.3. Characterization

Raman spectra of carbons deposited on the catalysts through ethanol decomposition were recorded by Almega Dispersive Raman spectrometer (Nicolet, ALMEGA) with excitation wavelength of 532 nm. X-ray diffraction (XRD, D/max-3c, Cu K_α, 50 kV, 300 mA, at room temperature in air) was used to characterize the compositions of the catalyst after reduction with hydrogen at 500 °C and the catalyst with solid products after ethanol decomposition. SEM (scanning electron microscopy) images of carbons deposited on the catalysts from ethanol decomposition were obtained with a FEI Quanta 400 FEG-ESEM (field emission gun-environmental scanning electron microscope). TEM (transmission electron microscopy) images of as-grown CNTs without any purification and pretreatment were carried out with a JEOL JEM-3010 electron microscope at 200 kV. Thermogravimetry (TG-DTG) analysis data were collected in a NETZSCH STA 449C instrument. The samples were heated from room temperature to 800 °C in air at a heating rate of 10 °C/min.

3. Results and discussion

Figure 1 shows SEM images of carbon products formed by ethanol decomposition over different Ni-Mo/MgO catalysts at 800 °C. The SEM images in Figure 1 indicate the morphology of CNTs was affected apparently by the loading ratio of Ni : Mo. As seen in Figure 1(a), CNTs can hardly form over Ni9Mo1 catalyst, the main solid product was amorphous carbon mixed with a few CNFs in the diameter range of 50−60 nm. Such a result suggests that Ni9Mo1 was not suitable for CNT growth. Different from Figure 1(a), the SEM image displayed in Figure 1(b) indicate the formation of dense CNTs (~25 nm in diameter) with few metal particles and a little amorphous carbon on Ni5Mo1 catalyst. For Ni1Mo1 catalyst, although CNTs can also be formed on it, the density of CNTs per unit area and the diameter of CNTs were both