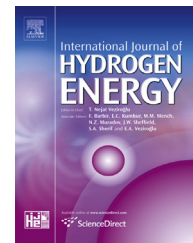




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Polyol synthesis of nickel–copper based catalysts for hydrogen production by methane decomposition

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ABSTRACT

A series of nickel–copper nanoparticles were synthesized using the polyol reduction method and examined as catalysts for hydrogen production by methane decomposition. The effects of surfactant polyvinylpyrrolidone (PVP), carbon nanotube (CNT) support and heterogeneous nucleation seed, i.e., H_2PtCl_4 solution on the structural and catalytic properties of the resulting catalysts were studied. The catalysts were extensively characterized using field scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and N_2 adsorption–desorption tests. The catalytic performance of the catalysts was evaluated in terms of methane conversion and carbon yield. It was found that the Ni–Cu alloying degree in the catalyst was critical to achieve high activity and that the catalytic performance was also closely related to the CNT support, the size and dispersion of the Ni–Cu particles. Among the catalysts, the Ni–Cu/CNT catalyst synthesized in the presence of PVP and H_2PtCl_4 solution exhibits the best catalytic activity with a stable methane conversion value of 0.8 and a carbon yield of $616 \text{ g C g}_{\text{Ni}}^{-1}$ at 700°C . The structures of the produced carbon materials were also characterized. Filamentous carbon nanofibers were obtained from the catalysts with high Ni–Cu alloying degrees while limited carbon lumps were generated from the catalyst with a low Ni–Cu alloying degree.

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Introduction

Due to the large consumption of fossil fuels, a series of environmental problems such as global warming, ozone layer

depletion, acid rain and air pollution are taking place. To address these issues, much work has been devoted to exploring renewable energy sources. Hydrogen is widely considered to be one of the most promising alternative clean fuels. Hence, numerous efforts have been directed in

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developing efficient, economic, and environmental-friendly approaches for hydrogen production [1–3]. Catalytic decomposition of methane (CDM) has been of great interest because only pure hydrogen and high quality carbon are obtained in this process [4–10]. CO_x-free hydrogen produced by the CDM process is favorable for fuel cell applications without further separation and purification. In addition, carbon is sequestered in the form of a stable valuable solid carbon nanotubes (CNTs) or nanofibers (CNFs) rather than carbon dioxide which is a notorious greenhouse gas.

It is well known that the CDM reaction is an endothermic process. High reaction temperatures are favorable for achieving high methane conversions and carbon yield rates. It has been demonstrated that some transition metals, such as Fe, Co and Ni, can effectively catalyze methane decomposition. In particular, among the three metals, Ni shows superior catalytic activity due to its unique 3d-orbital structures. However, the efficiency of nickel-based catalysts is significantly limited at low reaction temperatures. The sintering and encapsulation of nickel particles are inevitably observed at high reaction temperatures, resulting in low activity and stability. To enhance the operating temperature of Ni-based catalysts, one common strategy is to utilize some support materials such as Al₂O₃, SiO₂, MgO and TiO₂ [11–15]. It has been confirmed that the presence of catalyst support, not only promotes the dispersion of the active component, but also increases its stability, leading to significant increases in methane conversions and carbon yields. For instance, Takenaka et al. prepared 40 wt.% Ni/SiO₂ catalyst which showed a carbon yield of 491 g C g_{Ni}⁻¹ at 500 °C [12]. Nevertheless, supported Ni catalysts still suffer from deactivation at temperatures above 600 °C despite the presence of catalyst supports. Alternatively, the introduction of some promoter elements such as Mo, Cu, Rh, Pt and Pd, in the catalyst could significantly increase the operating temperature [16–19]. In particular, the introduction of Cu atoms in Ni crystals to form Ni–Cu based catalysts has been of great interest due to their superior activity and carbon yields [20–29]. Wang and Baker prepared the 2.4Ni–0.6Cu–1MgO catalyst by impregnation method, which resulted in a carbon yield of 456 g C g_{cat}⁻¹ at 665 °C [23]. Suelves et al. prepared a 78Ni–6Cu/16Al₂O₃ catalyst by a fusion method, which showed a carbon yield of 141 g C g_{cat}⁻¹ over 1 h at 700 °C [26]. Chen et al. prepared a 15Ni–3Cu–2Al₂O₃ catalyst by co-precipitation method, which resulted in a carbon yield of 630.6 g C g_{Ni}⁻¹ at 600 °C [27]. Reshетенko et al. prepared a 75Ni–15Cu–10Al₂O₃ catalyst, which showed a carbon yield of 700 g C g_{Ni}⁻¹ at 625 °C [21]. In addition, the 65Ni–25Cu/Nb₂O₅ catalyst reported by Li et al. showed a high carbon yield of 743 g C g_{Ni}⁻¹ at 600 °C [28]. Furthermore, Ashok et al. prepared a 60Ni–25Cu–15SiO₂ catalyst, which reached a maximum carbon yield of 801 g C g_{Ni}⁻¹ at 650 °C [29]. There is a general consensus that the introduction of Cu atoms can significantly modulate the electronic and surface properties of Ni crystals, which are responsible for the enhanced catalytic performance of Ni–Cu based catalysts at high reaction temperatures.

In the literature, Ni–Cu catalysts were most commonly prepared by impregnation, co-precipitation and fusion methods. These preparation methods involved two steps, i.e., calcination and reduction, to obtain the active metallic

particles. In contrast, the polyol reduction method is a one-step method to directly synthesize metallic particles. Despite the fact that the polyol reduction process has been widely utilized to synthesize metals such as, Pt, Cu, Ni, Co, Ag and alloys [30–33], so far, few studies have been reported on the catalytic activity of the resulting metal particles for CDM [34]. In this study, a series of Ni–Cu particles were synthesized using the polyol reduction method and further examined as catalysts for the CDM process. The effects of surfactant, CNT support and heterogeneous nucleation seed, i.e., H₂PtCl₄ solution, on the structural and catalytic properties of the catalysts were investigated.

Experimental

Purification of multi-walled carbon nanotubes

The carbon nanotubes (CNTs, Shenzhen Nanotech Port Co. Ltd. China) were purified to remove the metallic catalyst. The details of the procedure are as follows: 1 g of CNTs was added into 70 ml solution of concentrated nitric acid and sulfuric acid (volumetric ratio of 1:1). The CNTs were dispersed by ultrasonic waves for 30 min. The mixture was transferred into a 150 ml round flask and refluxed for 4 h at 120 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was carefully filtered and rinsed with water for three times. The purified multi-walled carbon nanotubes were dried and ground for further use.

Synthesis of catalysts

All the catalysts were synthesized using the polyol reduction method. The details of the procedure are as follows: 100 ml of ethylene glycol and 4 g of polyvinylpyrrolidone (PVP, Mw = 30,000) were introduced into a 150 ml beaker. After the complete dissolution of the surfactant, 0.25 g of purified CNTs was dispersed into the solution by alternate ultrasonication and magnetic stirring. 1.2 g of sodium hydroxide and 6 mmol of metal precursors, i.e., 4.5 mmol nickel (II) nitrate hexahydrate and 1.5 mmol copper (II) nitrate trihydrate, were added into the mixture. After the complete dissolution of the precursors, 250 μl of chloroplatinic acid solution (8 wt.%) was added into the mixture as the heterogeneous nucleation seed. It should be noted that the mole ratio of [PtCl₆]²⁻/([PtCl₆]²⁻ + Ni²⁺ + Cu²⁺) in the mixture was quite low (0.8%). Subsequently, the mixture was transferred into an oil bath and the reduction was carried out at 180 °C for 4 h under continuous magnetic stirring. After cooling to room temperature, the mixture was filtered and thoroughly washed with water and ethanol for several times. The resulting catalyst was dried at 80 °C overnight using a vacuum oven. To study the effects of surfactant PVP, support CNTs and heterogeneous nucleation seed, on the structural properties of the catalysts, another three catalyst samples were synthesized with varied conditions as shown in Table 1. For convenience, the catalysts were denoted as catalysts A, B, C and D in the following discussion. All the reagents for catalyst synthesis were obtained from Sigma Aldrich, Singapore and used as received.

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