



Effect of catalytic site position: Nickel nanocatalyst selectively loaded inside or outside carbon nanotubes for methane dry reforming

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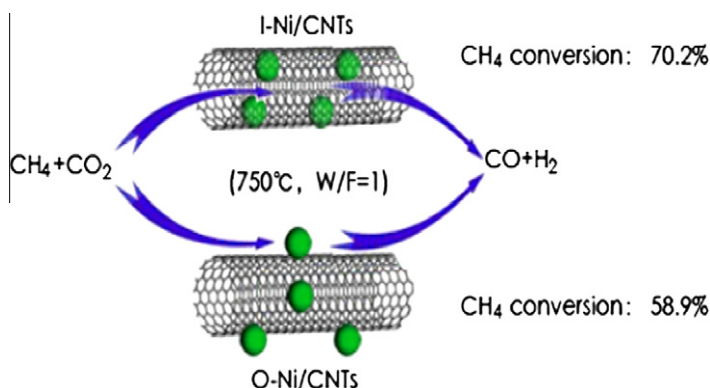
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HIGHLIGHTS

- ▶ Ni nanoparticles were selectively loaded inside or outside CNTs.
- ▶ Ni inside CNTs showed higher activity than Ni outside CNTs for methane dry reforming.
- ▶ Ni inside CNTs was more stable than Ni outside CNTs for methane dry reforming.
- ▶ Enhanced catalytic performance was attributed to the confinement of CNTs channels.

GRAPHICAL ABSTRACT

The catalysts with nickel nanoparticles selectively loaded inside or outside CNTs were prepared via wet chemical method and the catalytic performance was studied to clarify the different catalytic site position effect for methane dry reforming. The reaction results showed that I-Ni/CNTs had higher catalytic activity and better stability than O-Ni/CNTs.



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ABSTRACT

The catalysts with nickel nanoparticles selectively loaded inside or outside carbon nanotubes (CNTs) were prepared via wet chemical method to study the different catalytic site position effect such as inside and outside CNTs. The catalysts were characterized by N₂ adsorption, transmission electron micrographs (TEM), X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. TEM images and XPS demonstrated that most of nickel nanoparticles were controlled to be loaded at interior or exterior surface of CNTs. The H₂-TPR analysis results showed that the nickel oxide at the inside of the CNTs was easier to be reduced by H₂, which was attributed to the confinement effect of CNTs. Furthermore, this different reducibility resulted in an obvious different catalytic performance in terms of methane reforming of carbon dioxide. The reaction results demonstrated that the nickel catalyst with the nanoparticles inside CNTs exhibited higher catalytic activity and stability compared with the catalyst where nickel nanoparticles loaded outside CNTs.

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1. Introduction

Methane dry reforming has received significant attention in recently years, as the process of converted two greenhouse gases CH₄ and CO₂ to valuable syngas. The reaction equation is showed as following:



The dry reforming reaction is accompanied by several side reactions, such as the reverse water–gas shift reaction (2), the methane cracking reaction (3) and the Boudouard reaction (4) [1].



Compared to steam reforming of CH₄ or partial oxidation of CH₄ process, dry reforming of CH₄ has advantages in industrial demand for the production of syngas with H₂/CO ratio close to 1/1, which is more suitable for further synthesis of liquid hydrocarbon in Fischer–Tropsch synthesis on Fe-based catalyst and dimethyl ether (DME). Meanwhile, the dry reforming of methane was considered as one of the best way to store and transport solar or atomic energy.

In the previous reports, many VIII metals, such as Co, Ni, Rh, Ru and Pt, loaded on different supports have been used as catalyst for dry reforming reaction [2–9]. Nickel-based catalysts are more interesting than noble metal catalysts due to higher availability and lower price.

Recently, great attention has been paid to carbon materials with novel nanostructure such as carbon nanotubes, carbon nanofibers and carbon spheres. CNTs have unique properties such as large surface areas, mesopore structures, and uniform pore size distribution, resistance to high temperature, acid or base [10]. As a novel support material, CNTs were widely used as support material for catalytic reaction such as Fischer–Tropsch synthesis [11,12], higher alcohol synthesis [13,14], methanol synthesis [15], selective hydrogenation [16] and ammonia synthesis [17]. First-principles study revealed that deviation of the graphene layer from planarity caused π -electron density to shift from the concave inner surface to the convex outer surface, leading to an electron-deficient interior surface and an electron-enrich exterior surface. Furthermore, the different electronic properties between interior and the exterior CNTs lead to different catalytic performance when the catalyst was selectively loaded inside or outside CNTs [18]. Bao and Dalai compared the difference of catalytic site position between the interior and the exterior of the CNTs in Fischer–Tropsch synthesis [19,20]. They found that the catalyst filled inside CNTs presented lower reduction temperature than loaded outside CNTs, which was attributed to the different electronic properties of the inner and outer surface of the CNTs. According to their reports, the metal-support interaction inside CNTs channels may be different from that on the exterior surface of CNTs, which determined the difference catalytic performance.

In this report, the catalysts with nickel nanoparticles loaded inside or outside CNTs were prepared through wet chemical method, used for CO₂ reforming of CH₄, and the effects of catalytic sites position at interior or exterior surface of CNTs were investigated. TEM, BET, XRD, XPS, H₂-TPR, TG and Raman spectroscopy were employed to characterize the physicochemical property of the catalysts and the spent catalysts.

2. Experimental

2.1. Catalyst preparation

Raw multi-wall carbon nanotubes (inner diameter: 4–10 nm, Chengdu, China) (denoted as raw CNTs) were firstly refluxed in concentrated HNO₃ (65 wt.%) at 120 °C for 14 h, and then washed with deionized water until pH = 7. The sample was dried at 120 °C overnight (denoted as acid-treated CNTs). And then the obtained sample was further calcined at 900 °C under Ar atmosphere for 3 h (denoted as heat-treated CNTs). For the preparation of catalysts with Ni particles inside CNTs, catalyst was prepared by an improved wetness impregnation method. A certain amount of Ni(NO₃)₂ were dissolved in the ethanol solvent. Above treated CNTs with open ends was impregnated with the nickel solution and then vacuumed for 0.5 h. After ultrasonic treatment for 0.5 h, the sample was impregnated with deionized water and dried at 60 °C overnight. By this method, the particles could be easily deposited inside CNTs (denoted as I–Ni/CNTs). In order to prepare the catalyst with Ni catalytic site on the exterior surface of nanotubes, dimethyl benzene was used to fill the pore of nanotubes. The volume of the solvent was equal to the pore volume of CNTs. Then the nickel nitrate solution was added to the pore-filled support. After ultrasonic treatment for 0.5 h, the sample was dried at 60 °C overnight (denoted as O–Ni/CNTs). For the comparison of catalytic activity with the Ni/CNTs, the Ni/AC (active carbon) catalyst was prepared by wet impregnation method. A specified amount of Ni(NO₃)₂ was dissolved in deionized water. The amount of solution was equal to total volume of AC. Subsequently, the impregnated Ni/AC sample was treated by ultrasonic for 0.5 h and dried at 60 °C overnight.

All the samples were calcined in Ar at 450 °C for 3 h. Before the reaction, the catalyst was reduced at 500 °C for 2 h under a flow of 5% hydrogen of 40 ml/min. The loading of Ni for all catalysts was 10.0 wt.%.

2.2. Catalyst characterization

Nitrogen adsorption measurements were carried out at –196 °C under a Quantachrome Instruments AUTOSORB-1, and BET surface area and the pore size distribution were determined from the isotherms. The samples were outgassed at 200 °C for 2 h before each test. The samples were characterized by H₂ temperature programmed reduction (H₂-TPR) using BELCAT-B-TT (BELJAPAN INC.) in a flow system using 5% H₂/Ar mixture gases with 10 °C/min temperature ramp and with a flow rate of 30 mL/min. The power X-ray diffraction patterns were measured using Rigaku Corporation Instruments Rint2200 V/PC with monochromatized Cu/K α radiation. High resolution transmission electron micrographs (HRTEM) were obtained with a JEOL JEM-2100 UHR transmission electron microscope operated at 200 kV. Raman spectra were recorded with a Raman spectrometer using a laser excitation line at 514.5 nm. X-ray photoelectron spectroscopy (XPS) study was conducted using ESCALAB 250Xi spectrometer equipped with a monochromatized Al K α source focused to a spot size of 0.2 mm. The position of the C 1s peak (284.5 eV) was used to correct the binding energies for all catalysts for possible charging effects. The carbon deposition was characterized by thermogravimetric analysis using Shimadzu DTG-60 instrument. The spent catalyst was heated in a platinum sample cell in the air atmosphere from room temperature to 750 °C at a ramp rate of 10 °C/min.

2.3. Catalytic reaction

Dry reforming experiments were carried out in fixed-bed quartz reactor (6 mm i.d.) under atmospheric pressure. A reactant gas

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