



Preparation of meso-macroporous carbon nanotube-alumina composite monoliths and their application to the preferential oxidation of CO in hydrogen-rich gases

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ABSTRACT

A series of carbon nanotube (CNT)-alumina composite monoliths with meso-macroporous structures were successfully synthesized by imbibing macroporous monolithic polystyrene foams with carbon nanotube-alumina hydrosols. These composite monoliths possessed interconnected spherical macropores that mainly ranged in 10–40 μm and adjustable mesopores of several nanometers. CNTs were uniformly dispersed throughout the alumina matrix. The CNT content and the calcination temperature markedly influenced the mesoporous structure, mechanical strength and thermal conductivity of the composite monoliths, but they did not significantly influence the phase transitions of alumina. The Pt-Ni/CNT- Al_2O_3 monoliths that were calcined at 1300 $^\circ\text{C}$ exhibited high activity and selectivity with small Pt loading of 0.75 wt.% for the preferential oxidation of CO. The residual concentration of CO was purified to less than 100 ppm in the temperature range of 120–180 $^\circ\text{C}$ in CO_2 and water-containing hydrogen-rich gases at a volume space velocity of 10,400 h^{-1} . This type of composite monolith could potentially be used as a catalyst support for many different reactions.

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1. Introduction

The preferential oxidation (PROX) of CO in hydrogen-rich gases is considered to be a simple and cost-effective approach to purifying CO for proton exchange membrane fuel cells (PEMFCs) [1]. The H_2 -rich gases resulting from the catalytic reforming of hydrocarbons, which is typically followed by the water-gas shift reaction, contain 0.5–1.0 vol.% of CO. This level of CO must be decreased to less than 100 ppm to avoid electrode poisoning in the PEMFCs. Among the catalysts for CO-PROX, Pt-based catalysts [2], especially nickel- or cobalt-promoted platinum catalysts [3,4], are promising candidates. Conventional supports include CeO_2 [5], Al_2O_3 [6–8], SiO_2 [9], zeolite [10], and activated carbon [11]. The use of carbon nanotubes as a catalyst support has also been investigated [12,13], owing to their special structure, high mechanical strength, unique electronic properties and high thermal conductivity.

Recently, mesoporous and macroporous metal oxide materials have been the focus of widespread research for use in the fields of catalysis, separation, sensors, optics, and electronics [14–17]. With regard to their potential use as catalyst supports, their interconnected macropores can efficiently transfer reactant species, and their mesopores provide high surface area. However, drawbacks

include the relatively poor mechanical and thermal conductivities of oxide materials. If used as a catalyst support, the inferior thermal conductivity could lead to the formation of hotspots on the catalyst surface, which would induce the deactivation of the catalyst via active component sintering or the formation of byproducts through side reactions. The addition of CNTs to meso-macroporous oxides could be a possible approach to improve the mechanical and thermal conductivities of pure meso-macroporous oxides.

A composite of CNTs with meso-macroporous oxides should possess properties of both CNTs and meso-macroporous oxides, including high surface area, reasonable mass transfer, high thermal and electrical conductivity, and good mechanical strength. In addition, based on the differences in properties of the CNTs and the metal oxides, bi-functional materials could potentially be designed. Furthermore, the construction of a composite with a monolithic structure could lead to convenient and flexible applications. However, to the best of our knowledge, only one report describing this type of composite can be found. Worsley et al. [18] have fabricated a series of SWNT-CA (single-wall CNT-based carbon aerogel)/oxide (SiO_2 , SnO_2 , TiO_2) composites by depositing oxides onto the nanoligament surfaces of SWNT-CA monoliths. Their study concentrated on the electrical conductivity and mechanical properties of these composites.

Alumina is an oxide that is widely used as a catalyst support, adsorption material, ceramic material, and among others [7,19]. Studies focusing on mesoporous and meso-macroporous alumina

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have recently been attractive areas of interest [20–22]. Therefore, a study on the preparation of meso-macroporous CNT-Al₂O₃ composite monoliths should be a valuable and interesting contribution. Previously we found that CNTs supported Pt-Ni catalyst exhibited high activity and selectivity for CO-PROX [23]. Therefore, meso-macroporous CNT-Al₂O₃ composite monolith supported Pt-Ni may be a potential better alternative for CO-PROX.

In this work, meso-macroporous CNT-Al₂O₃ composite monoliths were prepared, characterized and used as a support for a CO-PROX catalyst. A simple preparation method involving a polystyrene foam template was used, and the influences of CNT content and calcination temperature on the properties of the composite monoliths were investigated. The prepared Pt-Ni/CNT-Al₂O₃-1300-M exhibited excellent catalytic performance for CO-PROX. The preparation approach described here provides a practical and simple method to synthesize porous, monolithic CNT-oxide composites, and the results suggest that this type of material possesses tremendous potential for future applications.

2. Experimental

2.1. Preparation of meso-macroporous carbon nanotube-alumina composite monoliths

The macroporous monolithic polystyrene (PS) foams were prepared using a method that was similar to one previously reported by our group [24]. The meso-macroporous carbon nanotube-alumina composite monoliths were synthesized by imbibing macroporous monolithic polystyrene foams with carbon nanotube-alumina hydrosols. Prior to use, the as-received aligned multi-walled carbon nanotubes (CNTs, 10–20 nm i.d. and 5–15 μm length) were oxidized with an H₂SO₄-HNO₃ mixture to increase their hydrophilicity, as previously described [23]. The resulting carbon nanotubes were denoted as CNTs-OX.

The carbon nanotube-alumina hydrosols were prepared as follows: 4 g of pseudo-boehmite was added into 30 mL of distilled water, followed by vigorous stirring at room temperature for 1 h. Then 6.8 mL of HNO₃ (2 mol L⁻¹) was added dropwise into the above suspension to form translucent alumina hydrosols. After stirring for 10 min, 30 mL of CNTs-OX that had been dispersed by ultrasonic agitation in distilled water was added to the alumina hydrosols. The mixture was allowed to continue stirring for 5 h.

Afterward, the PS foams were completely immersed in the carbon nanotube-alumina hydrosols under modest vacuum until no air escaped from the PS foams. Then the infused PS foams were transferred to a 60 °C drying oven for 12 h. The imbibing and drying procedures were repeated several times.

All composite monoliths were calcined at 600 °C for 4 h with a heating rate of 1 °C min⁻¹ under a stream of N₂ (30 mL min⁻¹). Some samples were further calcined under a stream of N₂ at 900, 1100 or 1300 °C for 2 h.

The meso-macroporous CNT-alumina composite monoliths were labeled as *x* wt.% CNT-Al₂O₃-*y*-M, where *x* is the CNT to Al₂O₃ weight ratio, which was 0.5, 1.0, 3.0, 5.0, or 15.0, *y* is the calcination temperature, which was 600, 900, 1100 or 1300 °C, and M represents the meso-macroporous and monolithic properties of the composite material.

For comparison, Al₂O₃-1300-M was also prepared as reported in our previous paper [24].

2.2. Preparation of catalysts

Pt-Ni/5 wt.% CNT-Al₂O₃-1300-M catalysts were prepared by wet co-impregnation with aqueous solutions of Pt(NH₃)₂(NO₃)₂ and

Ni(NO₃)₂·6H₂O. After impregnation, the catalysts were frozen at 0 °C and stored at 0 °C for 12 h. They were subsequently freeze-dried for 12 h under vacuum for further use. The weight amounts of Pt and Ni in the catalyst, measured with ICP-AES, were 0.75 wt.% and 0.35 wt.%, respectively.

2.3. Characterization

Nitrogen adsorption and desorption isotherms were measured on a micromeritics apparatus (Tristar3000) at -196 °C. The specific surface areas were calculated using the BET method, and the pore size distributions were calculated from the desorption branch of the isotherms using the BJH model. All samples were outgassed under vacuum at 200 °C for 4 h prior to analysis.

The Pt and Ni content of the prepared catalysts were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Vista-MPX, Varian).

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 0.15406 nm) at room temperature from 10.0° to 90.0° (scan rate = 5° min⁻¹).

Scanning electron microscopy (SEM) characterizations were performed on a Hitachi S4800 field-emission scanning electron microscope to observe the macroporous structures of the samples.

The morphologies of the catalysts were observed with transmission electron microscopy (TEM) on a Technai G² F20 microscope operated at 200 kV. Samples were pre-reduced at 300 °C in 62.5 vol.% H₂/N₂ for 2 h, finely ground to fine particles in a mortar and dispersed ultrasonically in ethanol. The well-dispersed samples were deposited onto a Cu grid covered by a porous carbon film for measurements.

The compressive strengths of the samples were measured using a Shimadzu DSS-25T universal testing machine. The samples were fixed with flat steel plates and closed with a circular head at a speed of 0.5 mm min⁻¹.

The thermal conductivity measurements were performed on XIATECH TC3010 thermal conductivity tester by the use of instantaneous heat ray method at room temperature.

2.4. Catalytic performance for CO-PROX

Catalytic performance tests were carried out on a continuous-flow fixed tubular reactor at atmospheric pressure. In each test, a piece of monolithic catalyst (6 mm length and 7 mm i.d.) was put into a temperature-resistant silicone tube, and the silicone tube was connected with two quartz tubes at both ends. Before the catalytic reaction, the as-dried catalyst was reduced at 300 °C for 2 h with 62.5 vol.% H₂ in N₂ at a heating rate of 10 °C min⁻¹. TPR results indicated that at this temperature nickel and platinum ions could be reduced to metallic form, for that the reduced platinum can catalyze the reduction of nickel ions [25]. The reaction mixture consisted of 1 vol.% CO, 1 vol.% O₂, 0–12.5 vol.% CO₂, 0–15 vol.% H₂O, and 50 vol.% H₂, with N₂ comprising the remainder of the balance. The total flow rate was 40 mL min⁻¹, corresponding to a volume space velocity of 10,400 h⁻¹ and a mass space velocity of 24,000 mL g_{cat}⁻¹ h⁻¹. The reaction temperature was monitored using a K-type thermocouple placed on the catalysts and was controlled with a temperature controller. The effluent gases were analyzed using an on-line gas chromatograph (GC, model SP-3420) equipped with a TCD and a column packed with 5 Å molecular sieves. An FID detector equipped with a methanator was used; thus, the CO detection limit was 1 ppm. The activities of the catalysts were evaluated on the basis of CO conversion. The selectivity of O₂ for CO oxidation was defined

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