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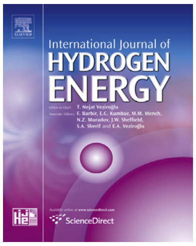

Morphology dependence of catalytic properties of Ni nanoparticles at the tips of carbon nanofibers for ammonia decomposition to generate hydrogen

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ABSTRACT

Ni nanoparticles at the tips of carbon nanofibers (Ni-CNFs) were synthesized by catalytic chemical vapor deposition (CCVD) method using CH_4 as the carbon source, and then employed as catalysts for the generation of H_2 from ammonia decomposition. The morphology of Ni catalysts is highly sensitive to the ratio of CH_4 to H_2. Especially for the CH_4/H_2 ratio of 4, the as-obtained Ni-CNFs catalyst shows higher H_2 formation rate, which could be due to more accessible facets to the reactants and unique shape effect. Meanwhile, this catalyst also shows good thermal stability, possibly owing to the highly dispersed and spatially isolated Ni nanoparticles by CNFs. Moreover, effect of the surface carbon coverage on the orientation of Ni crystal facets and the matching degree between graphene sheet and Ni crystal facet were investigated by DFT calculations. Finally, a possible formation mechanism of shaped Ni catalysts was discussed by combining experimental and theoretical results.

Introduction

The on-site and facile production of hydrogen is of paramount importance in many areas including environmentally clean alternative energy [1]. Generating H_2 via ammonia decomposition has recently attracted wide attention owing to the simplicity and efficiency of this process compared to the complex systems of methanol or hydrocarbon reforming [2,3]. Among the single-metal catalysts, Ru catalysts are the most active, but their high cost and limited availability are prohibitive to the large-scale applications [4–7]. Since ammonia decomposition catalysts are aimed for practical applications, the cost of the catalysts is crucial. Recently, researchers have made great efforts to develop low-cost alternatives to Ru catalysts, in which non-noble catalysts, especially Ni, are thought to be potential alternatives owing to both the low cost and the good activity though they usually work at higher temperatures than Ru catalysts [4–17].

Increasing the activities of Ni catalysts via tailoring the particle size and shape is of both fundamental and practical importance. Previous studies of the size effects show that the

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optimal Ni particle size is 2.3 nm for Ni/Al_2O_3 catalysts [18], while 3.1–3.6 nm for Ni/MCM-41 catalysts [19], indicating that ammonia decomposition over Ni catalysts is a typical structure-sensitive reaction. This sensitivity is most likely from the change in the ratio of Ni(111) to Ni(110) with the increase of Ni particle size, but not from the change in the number of B_5 sites, because the B_5 sites on Ni(211) surface are easily blocked by the adsorbed N* species [6,19]. Moreover, the shape effects of Ni catalysts show that the polyhedral Ni catalyst with sharp facets, prepared by CCVD method using CH_4 as the carbon source, has much higher activity than the pear-shaped one using CO as the carbon source [20]. However, the possible mechanism for the formation of Ni catalysts with controlled shapes is still unclear.

Another major concern of Ni catalysts is the thermal stability, because the Tammann temperature of Ni is ca. 590 °C and the commonly tested temperatures of Ni catalysts range from 300 to 700 °C. Ni will possibly suffer from the aggregation and subsequent sintering at higher reaction temperature. To this end, much effort has been made to enhance the stability of Ni catalyst by strengthening the interaction between Ni and supports, adding promoters and spatially isolating Ni particles by core–shell structure or carbon nanofibers [20–23].

In this work, we focus our attention on further design and optimization of Ni catalysts prepared by CCVD method for ammonia decomposition. In our previous work, changing carbon source using 15 wt% $Ni/\gamma\text{-}Al_2O_3$ as the initial catalyst was used to change the shape of resulting Ni catalysts, in which the kind of carbon source and the number of resulting C atoms simultaneously change [20]. As a consecutive effort, keeping the kinds of carbon sources unchanged, only the number of resulting C atoms is adjusted by varying the ratio CH_4 to H_2 in the feed gas, and a series of Ni catalysts with different shapes located at the tips of CNFs were prepared and tested for ammonia decomposition. Subsequently, the possible mechanism for the formation of Ni catalysts with controlled shapes is further explored by DFT calculations. This aims for understanding the formation mechanism of shaped Ni catalysts and the unique shape effects.

Experimental

Catalyst preparation

Ni catalysts at the tips of CNFs (Ni-CNFs) were in-situ synthesized through catalytic decomposition of CH_4 over 15 wt% $Ni/\gamma\text{-}Al_2O_3$ catalyst by CCVD method in a fixed-bed quartz reactor. In our previous work, the detailed procedures have been described [20]. Briefly, $Ni/\gamma\text{-}Al_2O_3$ catalyst was prepared using deposition–precipitation method with the n_{urea}/n_{Ni} ratio of 12. Ni-CNFs catalysts were synthesized over the reduced $Ni/\gamma\text{-}Al_2O_3$ catalyst by employing CH_4 mixed with H_2 at 600 °C for 4 h. The detailed synthetic conditions and the properties of various Ni-CNFs catalysts are summarized in Table 1.

Table 1 – Synthetic conditions and properties of various Ni-CNFs catalysts.

Samples	CH_4/H_2 (mL min^{-1}/ mL min^{-1})	Ni loading (wt%)[a]	Ni particle size (nm)[b]
Ni–CNF1	100/0	1.82	50.3
Ni–CNF2	90/10	1.83	50.0
Ni–CNF3	80/20	2.0	52.0
Ni–CNF4	60/40	2.7	54.1
Ni–CNF5	40/60	11.2	52.6
Ni–CNF6	20/80	13.7	23.0

[a] Ni loadings (referred to the total weight of Ni-CNFs) were determined by both the weight difference between the initial $Ni/\gamma\text{-}Al_2O_3$ catalyst and the as-obtained Ni-CNFs catalysts, and the thermal gravimetric analysis. The estimated loadings are similar by the two methods.

[b] Average sizes of Ni nanoparticles at the tips of CNFs were determined by FE-SEM measurements.

Catalyst characterization

The microstructure of the samples was determined by field emission scanning electron microscopy (FE-SEM, FEI NOVA Nano SEM 450, Netherlands) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, Japan). Raman spectroscopy was measured using a Raman microscope (Renishaw inVia Reflex, UK) with 2.41 eV excitation laser energy (wavelength of 514.5 nm) and laser power of 20 mW. Thermal gravimetric–differential thermal analysis (TG-DTA) was conducted with a flow of air in the temperature range 30–800 °C (heating rate: 10 °C min^{-1}) on a Pyris 1-TGA apparatus (Perkin–Elmer, USA). The crystal structure of the Ni-CNFs catalysts were examined by Powder X-ray diffraction (XRD) on a Rigaku D/Max2550VB/PC X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.54056$ Å). Notably, the reduced $Ni/\gamma\text{-}Al_2O_3$ catalyst was passivated in a stream of 0.98 vol% O_2/Ar at room temperature for 1.0 h before HRTEM and XRD characterizations.

Computational details

All calculations were conducted by the periodic spin-polarized DFT using GGA-PBE functional [24,25] and projector-augmented wave potentials [26] as implemented in the Vienna Ab-initio Simulation Package (VASP) [27–30]. The solution of the Kohn–Sham equations was expanded in a plane wave basis set with a cutoff energy of 400 eV, and the sampling of the Brillouin zone was performed using a Monkhorst–Pack scheme [31]. Electron smearing was employed via the Methfessel–Paxton technique with a smearing width consistent to 0.2 eV [32]. A minimum was considered to be converged when the maximum force in every degree of freedom was less than 0.03 eV $Å^{-1}$. The methods reported by Huo et al. [33] and Ji et al. [34] were employed to calculate the surface energies of clean and carbon adsorbed Ni(100), Ni(110), Ni(111) and Ni(211) surfaces, in which the detailed parameters of the slab models are shown in Table S1. In addition, the detailed parameters of the slab models for graphene sheet on different Ni crystal facets are listed in Table S2.

Catalytic testing

Catalytic testing of the as-obtained Ni-CNFs catalysts (ca. 0.1 g) was carried out in a tubular continuous flow quartz

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