

Novel Catalysts for the Production of CO_x-free H₂ and Carbon Nanotubes by Non-oxidative Dehydrogenation of Methane

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Introduction

Hydrocarbon decomposition is an alternate route for producing CO_x-free hydrogen that will satisfy the major requirement for successful utilization of polymer electrolyte membrane (PEM) fuel cells. In previous work, Fe-M (M= Pd, Mo, Ni) bimetallic catalysts on γ -Al₂O₃ supports prepared by traditional methods, such as impregnation and incipient wetness, were developed by our research group for catalytic dehydrogenation of lower alkanes. The catalysts lowered the decomposition temperature of methane by 400-500 °C and achieved ~70-90% conversion of undiluted methane into pure hydrogen and multi-walled carbon nanotubes at 650-800 °C with a space velocity of 600 ml·hr⁻¹·g⁻¹. However, the particle size distribution of the catalysts could not be well controlled and it was difficult to clean the potentially valuable carbon nanotubes (CNT) product because of difficulty in dissolving alumina support. Here, we introduce a new approach of synthesizing methane dehydrogenation catalysts by nanoparticle inclusion technique. These catalysts exhibited longer life-times and yielded higher quality carbon nanotubes after washing with nitric acid.

Materials and Methods

First, the monodisperse catalyst nanoparticles (np) were prepared by thermal decomposition of a metal-organic complex in an organic-phase solution. The high surface area MgAl(O) support was prepared separately by calcination of synthetic MgAl-hydrotalcite at 550°C for 5 hours. Known quantities of nanoparticles were “included” on the support to produce the methane dehydrogenation catalyst. The catalytic dehydrogenation reaction was conducted in a fixed-bed plug flow reactor. The collected CNTs were purified in 6 M HNO₃ solution at room temperature or at reflux condition followed by washing with deionized water.

Results and Discussion

The undiluted methane dehydrogenation reactions were conducted at three temperatures, 600°C, 650°C and 700°C, with catalyst loading of 0.2 gram for each experiment. The results were compared with the catalytic performance of a Fe-Ni/Mg(Al)O catalyst prepared by incipient wetness (IW) method with catalyst loading of 1 gram. The Fe-Ni np catalyst exhibits higher hydrogen production and longer lifetime than the IW Fe-Ni catalyst, despite having only one-fifth the amount of catalyst loading. Particularly at 600°C, the Fe-Ni np catalyst produces nearly 60 volume % hydrogen in the effluent stream with very little decrease in activity over the five-hour time-on-stream (TOS) period. The CNT products are in the form of multi-walled nanotubes (MWNT) at all three reaction temperatures. The same reaction was conducted by using Fe np /MgAl(O) catalysts with different particle sizes of 4 nm and 12 nm. Decreasing the nanoparticle size dramatically enhances the catalyst performance for methane dehydrogenation reaction. XAFS and Mössbauer spectroscopic studies reveal that FCC structured Fe or FeNi alloy is the catalytically active phase. Alloying with Ni appears to

stabilize the FeNi FCC phase, which in turn improves the catalyst life-times. The deactivation of catalyst is believed to be due to the formation of Fe-C or Fe-Ni-C phases. The prepared CNTs can be easily purified by washing with 6M HNO₃ solution at room temperature.

Significance

Catalysts prepared by the np inclusion method, rather than the IW method, help to better control both particle size and composition. These catalysts show higher hydrogen production and longer life times than the traditional catalysts. Using this new class of catalysts, scientists could generate large quantities of pure hydrogen in one step for the hydrogen economy, while recovering higher quality nanotubes as by product.

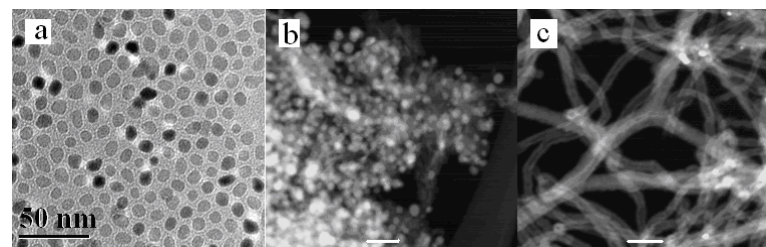


Figure 1. (a) Monodispersed FeNi Nps (TEM); (b) FeNi np/MgAl(O) activated (STEM); (c) CNTs produced over FeNi np/MgAl(O) catalyst at 600 °C for 5 hours (STEM). (scale bar: 50 nm)

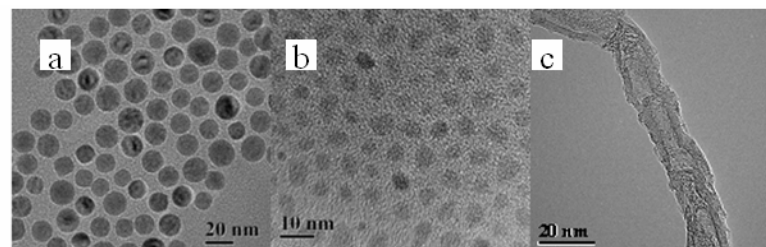


Figure 2. TEM images of: (a) Monodispersed Fe-12nm Nps; (b) Monodispersed Fe-4nm Nps; (c) MWCNT produced over Fe-4nm/MgAl(O) catalyst at 600°C for 5 hours.

References

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