Development of Highly Active Nanoscale Catalysts for Production of CO Free Hydrogen by Dehydrogenation of Methane

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Abstract:

Hydrocarbon decomposition is an alternate route for producing CO-free hydrogen that will satisfy the major requirement for successful utilization of polymer electrolyte membrane (PEM) fuel cells[1, 2, 3]. In previous work, Fe-M (M=Pd, Mo, Ni) bimetallic catalysts on γ-Al_2O_3 supports prepared by traditional methods, such as impregnation and incipient wetness, were developed by our research group for methane catalytic decomposition. The catalysts lowered the decomposition temperatures of methane by 400-500 ºC and achieved ~70-90% conversion of undiluted methane into pure hydrogen and multi-walled carbon nanotubes at 650-800 ºC with a space velocity of 600 $mlhr^{-1}g^{-1}$. However, the metal particle size of the catalysts could not be well controlled and it was difficult to clean the potentially valuable carbon nanotube (CNT) product because of the difficulty of dissolving the alumina support. The objective of this research, therefore, is to develop novel catalysts for non-oxidative dehydrogenation of methane to produce CO- and CO_2- free H_2 with high quality carbon nanotubes (CNT) as potentially valuable by-product. The Mg(Al)O support was prepared by calcination of a hydrotalcite-like precursor, $Mg_5Al(OH)_{11}CO_3 \cdot xH_2O$, at 550ºC for 5 hours. The N_2 adsorption-desorption isotherms, XRD, and TEM show that the support has large external surface area (about 180 m^2/g) due to nanoscale Mg(Al)O crystal particles (4 to 6 nm), which make it an excellent sorbent for catalyst nanoparticles. Additional, the basicity of the support makes it easy to dissolve in dilute nitric acid, which greatly simplifies the purification of the produced CNT.

A novel Fe-Ni catalyst was prepared by the method of nanoparticle (np) inclusion, in which synthesized 12 nm $Fe_{65}Ni_{35}$ particles (molar ratio, total loading 5 wt.%) were adsorbed onto the surface of the Mg(Al)O support under sonication[4, 5]. A second Fe-Ni bimetallic catalyst with the same metal loading (5 wt.%) and Fe/Ni ratio was also prepared by a conventional incipient wetness (IW) method for comparison. The performance of these two catalysts for methane dehydrogenation is compared in Fig. 1 and Fig. 2. The reaction was conducted in a fixed-bed plug flow reactor with a methane flow rate of 10 ml/min. Before reaction, the catalysts were activated by programmed reduction in a H_2 atmosphere. Fig. 1 shows the time-on-stream (TOS) H_2 production over the novel Fe-Ni np/Mg(Al)O catalyst. The reaction was conducted at three temperatures, 600ºC, 650 ºC and 700ºC, with total catalyst loading of 0.2 gram. Fig. 2 presents the catalytic behavior of the IW Fe-Ni/Mg(Al)O catalyst at 500ºC, 650ºC and 700ºC with total catalyst loading of 1 gram, 5 times that of the novel catalysts. The Fe-Ni np catalyst clearly exhibits much better hydrogen production and lifetime than the IW Fe-Ni catalyst, despite having only one-fifth the amount of catalyst loading. At 600 ºC, the Fe-Ni np catalyst behavior is particularly good, exhibiting nearly 60% hydrogen production with very little decrease in activity over the five-hour TOS period. The CNT products are in the form of multi-walled nanotubes (MWNT) at these temperatures. At 700 ºC, both catalysts deactivate very quickly, suggesting a change in the structure of the catalyst. After reaction, even at 700ºC, no evidence of sintering or agglomeration of the Fe-Ni nanoparticles was observed by TEM.

The differences between these two catalysts have also been studied by surface techniques, such as TEM, STEM, and elemental mapping. The catalyst particles prepared by incipient wetness have a broad size distribution with two size regimes due to the Oswald ripening effect. However, by using the nanoparticle inclusion method, we can control the catalyst particle size to a desired value, producing nearly monosized catalyst nanoparticles. This not only improves the catalytic performance, it also makes the diameter of the produced CNT more uniform. XAFS and Mössbauer on-going spectroscopic studies are being employed to reveal details of the mechanism of catalytic activity and deactivation of the Fe-Ni np/Mg(Al)O catalyst. More details will be presented in a publication now in preparation[6].
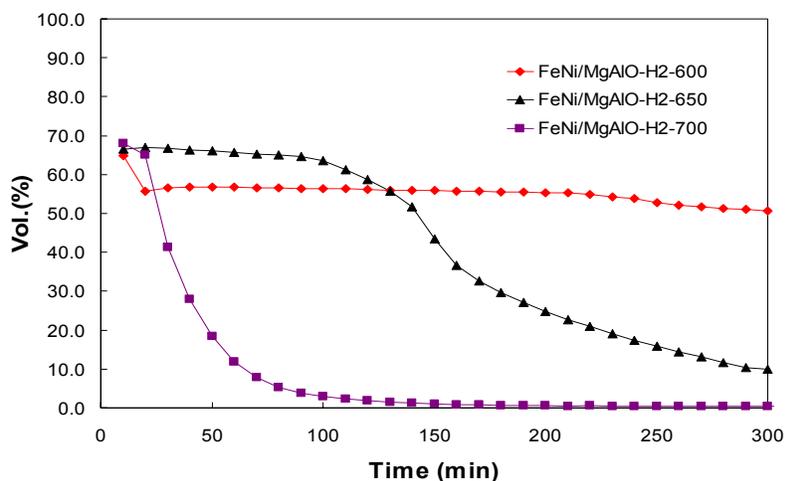
Fig. 1. Time-on-stream H_2 production distribution with 0.2 gram of $Fe_{65}Ni_{35}$ (12 nm)/Mg(Al)O catalyst at different temperatures
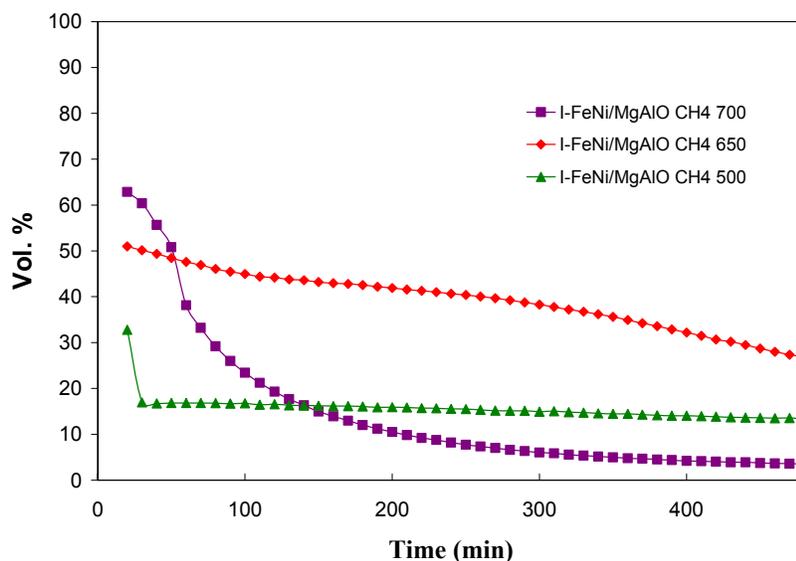
Fig. 2. Time-on-stream H_2 production distribution with 1.0 gram of IW $Fe_{65}Ni_{35}$/Mg(Al)O catalyst at different temperatures

In the near future, efforts will be directed in our lab to preparing $Fe_{65}Ni_{35}$ np catalysts with sizes of 4 to 5 nm, which should lead to longer lifetimes and higher activity for methane decomposition at relatively low temperature. We also plan to examine the effect of the Ni content in FeNi nanoparticles on catalytic performance.

[1] N. Shah, D. Panjala, and G. P. Huffman, Energy & Fuels, 15, 2001, 1528

[2] N. Shah, Y. Wang, D. Panjala, and G. P. Huffman, Engergy & Fuels, 18, 2004, 727

[3] R. Guil-López, V. La Parola, M. A. Peňa, J. L. G. Fierro, Catal. Today, 116, 2006, 289

[4] J. Park, K. An, Y. Hwang, J-G. Park, J-J. Noh, J-Y. Kim, J-H. Park, N-M Hwang, and T. Hyeon, Nature Materials, 3, 2004, 891

[5] K. Niesz, M. M. Koebel, G. A. Somorjai, Inorgnica Chimica Acta, 359, 2006, 2683

[6] W. Shen, Y. Wang, X. Shi, N. Shah, F. Huggins, G. Huffman, " Synthesis of Fe-Ni nanoparticles for catalytic dehydrogenation of methane for CO-free H_2 production", in preparation.