Lanthanum nickelate-perovskite: Catalyst for production of CO_x-free hydrogen and carbon nanotube from decomposition of CH_4

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Introduction

Hydrogen is expected to become an efficient source of an ultra-clean energy. Currently, reforming or partial oxidation of methane is the most widely used to produce hydrogen. However, these processes also produce CO and CO_2 which are considered as toxic and pollutant gases. An interesting alternative process is the catalytic decomposition of methane (CDM) (CH_4 —>C+$2H_2$) whereby the formation of CO and CO_2 is completely avoided. Moreover, the carbon deposited in the useful form of fiber or nanotube which is of great interest in nanotechnology due to the unique electric, chemical and mechanical properties of carbon nanotube. It is well-known that Ni- supported catalyst is one of the promising catalysts for CDM to form carbon nanotubes (CNTs) [1]. However, the catalytic life of Ni-supported catalysts for CDM was relatively short due to the formation of large Ni^0 particles on support [2]. Thus, a catalyst containing very small Ni^0 particles is required in order to attain high activity and stability. It is well-known that lanthanum nickelate-perovskite ($LaNiO_3$), which contains reducible Ni^{3+}, the reduction under H_2 can form nanosized Ni^0 particles well-dispersed on La_2O_3 [3].

In this work, we have investigated the effects of the structure of La-Ni-O catalyst system (i.e. $LaNiO_3$ perovskite and Ni/La_2O_3) and the reaction condition on their catalytic performance for co-production of hydrogen and carbon nanotubes (CNTs) from CDM.

Materials and Methods

$LaNiO_3$ perovskite was prepared according to Pechini method [3], while Ni/La_2O_3 with the same amount of Ni (24wt% Ni) was prepared by wet impregnation. $Ni(NO_3)_3.6H_2O$, $La(NO_3)_3.6H_2O$ and La_2O_3 were used as starting materials. The obtained catalysts were characterized by XRD, H_2-TPR, BET and SEM. The catalytic activity was then studied in a horizontal-reactor. All catalysts were reduced under H_2 atmosphere at 600°C for 1.5 h before the reaction was performed at the methane pressure of 2 atm and reaction temperatures between 500 – 800˚C. The used catalysts were finally characterized by SEM, TEM, XRD and others.

Results and Discussion

Figure 1 shows the production of H_2 (volume %) with time on stream from CH_4 decomposition over $LaNiO_3$ and 24-wt% Ni/La_2O_3 catalysts at 700°C. The result shows the same catalytic activity at the early stage of the reaction as both catalysts have the same amount of Ni. However, after that the activity of 24-wt% Ni/La_2O_3 rapidly declined from 80 to 30 vol% H_2, while the activity of $LaNiO_3$ was fairly constant at 75-80vol% H_2 within 7 h. These results indicate that the hydrogen reduction of $LaNiO_3$ formed highly-dispersed Ni^0 particles on La_2O_3, leading to the enhancement of the catalytic life and hydrogen yield of $LaNiO_3$ for CDM.

Figure 2(a) shows that the $LaNiO_3$ catalyst is completely covered by a large amount of CNTs after 7 h, while less amount of CNTs are observed on the 24-wt% Ni/La_2O_3 catalyst (Figure 2(b)). These results indicate that the formation of CNTs allow the catalyst to maintain its activity for CDM. Figure 2(c) shows the mechanism for the formation of CNTs on Ni^0 particles on the reduced $LaNiO_3$. This result is similar to the proposed mechanism reported in the literature [1]. Decomposition of CH_4 occurs on the front surface of Ni^0 particle, followed by the dissolution of carbon atom into the particle, diffusion through the particle, and finally precipitation at the rear surface in the form of nanotube. This mechanism allows $LaNiO_3$ catalyst to maintain its activity for an extended period of reaction time without deactivation.

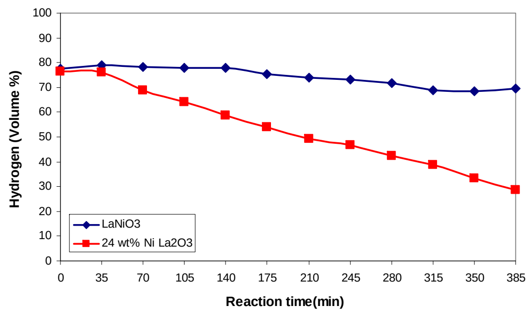

Figure 1. Time on stream (TOS) H_2 production over $LaNiO_3$ and 24-wt% Ni/La_2O_3 at 700°C

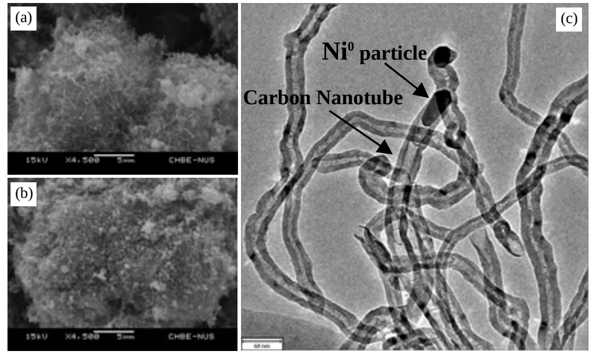

Figure 2. (a), (b) SEM images of used $LaNiO_3$ and 24-wt% Ni/La_2O_3, respectively and (c) TEM image of the produced CNT from $LaNiO_3$.

Significance

1. $LaNiO_3$ perovkite can enhance both catalytic activity and stability for catalytic decomposition of methane because it can provide very small and well-dispersed Ni^0 particles on La_2O_3 after reduction.
2. The highest performance of $LaNiO_3$ for the highest production of hydrogen and CNTs can be obtained at the reaction temperature around 700°C.

References

1. Ruckenstein, E., and Hang H.Y., *Carbon* 36, 269 (1998)
2. Takenaka, S., Shigeta, Y., Tanabe, E., and Otsuka, K., *J. Phys. Chem. B* 108, 7656 (2004).
3. Gallego, G.S., Fanor, M., Barrault, J., Jean, M.T., and Catherine B.D., *Appl. Catal. A: General* 311, 164 (2006).