Effect of Ag and W in nickel based catalyst for methane reforming

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Abstract: In the present study, co-impregnated tungsten and silver onto nickel based catalysts have been investigated. By adding trace of tungsten subsidiary to silver, it was able to reach as high performance as the catalyst with silver only. The influences caused by tungsten modification were inspected by XRD, XPS, TPR and TEM with Elemental Mapping from SEM. the result revealed similarity in terms of physicochemical properties.

Keywords: Methane reforming, Nickel catalyst, Silver.

1. Introduction (11-point boldface)

Gas to liquid is a promising technology due to its flexibility in product (LPG, Naphtha, Normal Paraffin, Kerosene, Gasoil, Base Oil, Wax etc.).[1] GTL plant includes several steps but among them, reforming process accounts for more than 50% of its cost. Many researchers have studied about the process in various perspectives. The subject related to the catalyst has actively been investigated since catalyst is necessary to the reaction lowering its energy consumption. Nickel catalyst is known as one of the best commercial candidates due to its reactivity to methane. However, Ni also entails drastic deactivation by sintering and carbon deposit. In order to overcome the demerit, Ni is usually used with other promoters. In this study, we suggested adding small amount of W in replacement of Ag, noble metal, for the sake of showing almost identical stability but still holding price competitiveness for the industrial usage.

2. Experimental (or Theoretical)

2.1. Catalyst preparation

All catalysts for the reaction have been made by co-impregnation method. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Junsei Chemical Co., Ltd, 97%), Silver nitrate ($AgNo_3$, Sigma Aldrich, 99.9999%), Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, Yakuri Chemical Co., Ltd, Extra pure) were used as the precursor and 1 mm ball type) γ-Al_2O_3 (BET surface area = 140 m^2/g; Sasol product) was used as a support. The precursors was mixed with 20ml distilled water and stirred for a half hour. Then the solution was moved into evaporator and mixed with supports for an hour. The mixture was evaporated under vacuum, 50°C. After complete evaporation, the balls were dried in 100 °C of oven for a day and then calcined under the temperature of 800°C for 4hr. Every catalyst had prepared in same process with 10wt% of Ni and different loading amount of other metals. The catalysts were labeled as Ni, Ni-Ag0.16, Ni-Ag0.16-W0.8, Ni-Ag0.5 by its kind of the metal and the loading weight percent. All prepared catalysts were characterized by XRD (Rigaku, Japan, DMAX100), H_2-TPR(BEL-CAT, BEL, Japan), TGA(TGA-50, Shimadzu, Japan) and TEM(JEOL, Japan).[2]

2.2. Activity test

Methane reforming was conducted with fixed bed reactor (i.d. 10.2mm, length 300mm). Catalyst bed was composed with 0.3g of catalyst with quartz wool between the catalyst and K-type thermocouple. Before the reaction, catalyst went through reduction process for activation. The reaction was carried out under the condition of 40000 cm^3/gcat-h, 20bar, 900°C. Inlet gas has a ratio of $CH_4 : H_2O : CO_2 = 1 : 0.7 : 1.5$ and Ar was used as a carrier gas. Outlet gas was examined by GC (HP 5890 series II) –TCD.

3. Results and discussion

As shown in Table I, Ag addition lessen the activity of catalysts. it is due to the fact that Ag locates on the step sites of Ni which lead high reaction rate of CH4.[5] Ni step site has improved reactivity compared to Ni terrace site.[4,5] Ag on Ni step site hinders the reactant so that it affect in both way, reducing the activity and the possibility of coke accumulation. Instead of adding 0.5wt% of Ag, the activity has improved by reducing Ag amount and adding a trace of W in Table I. The result suggests W doping can be an effective method to enhance coke resistance while maintain the catalyst activity.

Catalyst	**CH_4 conversion**	**CO_2 conversion**	**H_2/CO**
Ni	89.3	44.1	2.2
Ni-Ag0.16	81.5	40.5	2.2
Ni-Ag0.16-W0.8	84.8	43.6	2.3
Ni-Ag0.5	69.2	37.3	2.1

Table 1. CH_4 and CO_2 conversion and H_2/CO ratio for 8 h time on stream under 900 ℃, 20bar

Ag added catalysts show enhanced coke resistance.[6] The more Ag added, the less coke obtained. Ni Ag0.16-W0.8 shows almost similar resistance to Ni-Ag0.5 even though it contains lesser Ag amount.

In order to determine the reason for its higher coke resistance, TEM analysis was conducted. Figure 2 displays the TEM image of each catalyst and Figure 2A and B show clear dark area as opposed to Figure 2C.

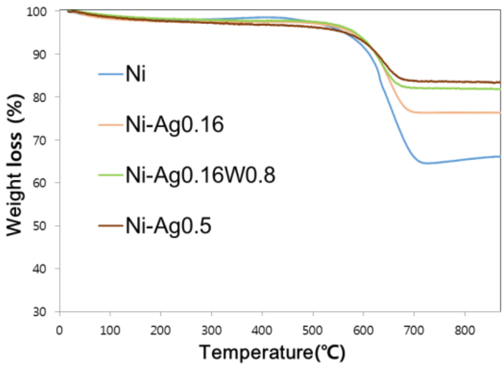

Figure 1. TGA analysis of used catalysts

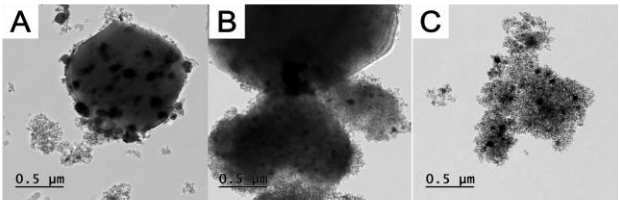

Figure 2. TEM images of A) Ni-Ag0.5, B) Ni-Ag0.16-W0.8 and C) Ni-Ag0.16 catalyst after reaction

4. Conclusions

As shown in Table I, Ag addition lessen the activity of catalysts. it is due to the fact that Ag locates on the step sites of Ni which lead high reaction rate of CH4.[14] Ni step site has improved reactivity compared to Ni terrace site.[15, 16] Ag on Ni step site hinders the reactant so that it affect in both way, reducing the activity and the possibility of coke accumulation. Instead of adding 0.5wt% of Ag, the activity has improved by reducing Ag amount and adding a trace of W in Table I. The result suggests W doping can be an effective method to enhance coke resistance while maintain the catalyst activity.

References

1. J. Cha, *repseat report* (**2004**). one author
2. L. Liu, S. Wang, Y. Guo, B. Wang, P. Rukundo, S. Wen, Z. Wang, *Int. J. Hydrogen Energy* 41, 17361 (**2016**). many authors
3. H.S. Bengaard, J.K. Nørskov, *J. Catal.* 209, 365 (**2002**). two authors
4. F. Besenbacher, I. Chorkendorff, *Science* 279, 1913 (**1998**). two authors
5. M. Yu, Y. Zhu, Y. Lu, G. Tong, K. Zhu, X. Zhou, *Appl. Catal. A* 165, 43 (**2015**). many authors