

## Catalytic steam reforming of coke oven gas for hydrogen production

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### Introduction

Coke oven gas(COG) by-produced from coke making process is considered as a promising raw gas for producing hydrogen in the future since it contains large proportions of hydrogen(>50% in volume) and light hydrocarbon gases, mainly, methane(25%) [1]. Pure hydrogen has been separated from cold clean COG by employing pressure swing adsorption (PSA) process although hydrogen amplification by the reforming of light hydrocarbons is not performed. Recently, the catalytic or thermal reforming of tar using the heat from the hot crude COG (~800°C), containing tar, methane, etc., has been researched to amplify hydrogen or synthesis gas with a recoverable energy [1, 2]. However, the former catalytic reforming of hot crude COG has several difficult problems to solve, such as severe carbon-coking or/and H<sub>2</sub>S poisoning, and the latter thermal reforming commonly uses an extra heating by oxygen feeding, which cannot achieve high yields of synthesis gas. Due to the drawback, it is thought that much hydrogen gas can be produced from the cold clean COG without H<sub>2</sub>S, tar and light oil after cleaning processes such as aqueous ammonia quenching [1].

The goal of the present study was to systematically investigate the reforming reaction of the clean COG gas containing methane, CO, CO<sub>2</sub>, and so on, with steam or/and CO<sub>2</sub> over several Ni-based catalysts and theoretically evaluate the economic feasibility for H<sub>2</sub> production from COG compared to LNG reforming by means of Aspenplus program.

### Materials and Methods

Ni/MgO/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a simple impregnation method, where different precursors of alumina support including  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (ox) and Al(OH)<sub>3</sub> (hy) were used. The methane reforming activities of the samples prepared and commercial Ni catalysts (co) have been examined within the reaction temperature of 700~900°C by a fixed-bed flow reactor. A total flow rate of 300 cc/min of COG generated by MFC, consisting of CH<sub>4</sub>, H<sub>2</sub>, CO, and CO<sub>2</sub>, was usually employed for the catalyst activity test, corresponding to GHSV = ca. 70,000 h<sup>-1</sup>. The Ni-based catalysts prepared have been characterized by XRD, TPR, BET, etc., to understand the COG-reforming process. And the material and energy balances of the COG-reforming process were calculated by Aspenplus to evaluate the economic feasibility of H<sub>2</sub> production from COG.

### Results and Discussion

The activities of the Ni-based catalysts for the reforming of CH<sub>4</sub> to CO and H<sub>2</sub> have been examined in COG containing H<sub>2</sub> (57%), CH<sub>4</sub> (30%), CO (8%), and CO<sub>2</sub> (5%) as shown in Figure 1. It is clear that Ni/MgO/Al<sub>2</sub>O<sub>3</sub> showed better activity in the reaction temperature than

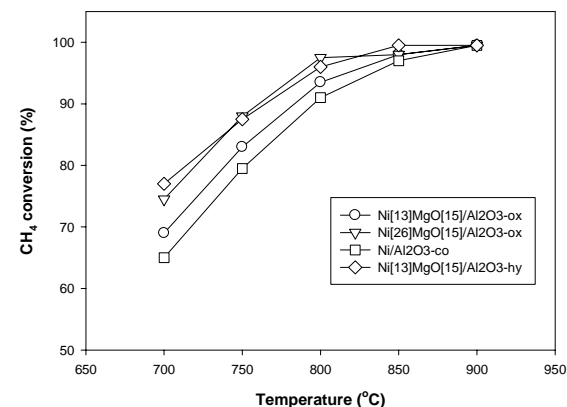
Ni/Al<sub>2</sub>O<sub>3</sub>(co), particularly, in the low reaction temperature. At 700°C Ni/MgO/Al<sub>2</sub>O<sub>3</sub>(hy) showed 76% CH<sub>4</sub> conversion. On the contrary, Ni/MgO/Al<sub>2</sub>O<sub>3</sub>(ox) and Ni/Al<sub>2</sub>O<sub>3</sub>(co) showed CH<sub>4</sub> conversion of 70 and 63%, respectively. The promoted activity of Ni/MgO/Al<sub>2</sub>O<sub>3</sub>(hy) may be related to Ni state and coke formation, which is confirmed by XRD, TPR, BET, etc.

Their activity patterns are nearly similar to those of CH<sub>4</sub> reforming, regardless of the difference of their reactant composition. It is indicating that the reforming reaction under COG mainly depends on the thermodynamic equilibrium. These results strongly suggest that the steam reforming of clean COG over Ni/MgO/Al<sub>2</sub>O<sub>3</sub>(hy) can be performed efficiently.

The steam COG reforming for hydrogen production has also been investigated to evaluate the economic feasibility by thermodynamic analytic tool-Aspenplus. The thermodynamic equilibrium in the reforming reactor was calculated by the minimization of the Gibbs free energy. Simulated material and energy balances show that the COG reforming process is profitable in the CO<sub>2</sub> emission and the cost of H<sub>2</sub> production compared to that of LNG reforming process.

### Significance

The present study systematically examined COG reforming over Ni-based catalysts and assessed the economic feasibility of H<sub>2</sub> production from COG.



**Figure 1.** CH<sub>4</sub> conversion for COG reforming over (○) Ni[13]MgO[15]/Al<sub>2</sub>O<sub>3</sub>-ox, (▽) Ni[26]MgO[15]/Al<sub>2</sub>O<sub>3</sub>-ox, (□) Ni/Al<sub>2</sub>O<sub>3</sub>-co, and (◇) Ni[13]MgO[15]/Al<sub>2</sub>O<sub>3</sub>-hy: the numbers in parenthesis [ ] are the weight percent of the component.

### References

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2. Liuyun, L., Morishita, K., and Takarada T. *Proceedings of 12<sup>th</sup> International Conference on Coal Science*, Cairns, Australia (2003).