Effect of Ba addition on Ni/Al_2O_3 catalyst for the steam reforming of naphthalene/benzene as tar model compounds

Yoshito Inagawa, Koshiro Iimura, Takeshi Furusawa*, Masahide Sato, Noboru Suzuki

Department of Material and Environmental Chemistry, Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan

Corresponding author: T. Furusawa, Fax; +81-(0)28-689-6160, E-mail; furusawa@cc.utsunomiya-u.ac.jp

Abstract: Effect of Ba addition on the catalytic performance of Ni/Al_2O_3 catalyst for the steam reforming of naphthalene/benzene derived from the steam gasification of woody biomass was investigated. The results indicated that the catalytic activity obtained at 923 K with S/C molar ratio of 3 was increased from 80% to 100% with Ba addition. Moreover, it was revealed for Ba-Ni/Al_2O_3 catalyst that the amount of carbon deposited on the tested catalyst was remarkably decreased, and CO selectivity was improved in the steam reforming during 5 h of reaction.

Keywords: Ba-Ni/Al_2O_3 catalyst, steam reforming of tar, carbon deposition

1. Introduction

Biomass steam gasification offers great potential for alleviating global warming and fossil fuels problems because biomass is a carbon neutral resource[1]. The effluent gas from steam gasification of woody biomass contains variable amounts of ash particles, volatile alkali metal and condensable aromatic hydrocarbons (tar). As tar causes many problems such as pipe plugging in gasification system and downstream equipments, the tar removal process is necessary step to operate the system smoothly[2]. From these backgrounds, our research group also investigated the development of the catalysts applied for tar removal and had been reported that Pt-based and Ni-based catalysts showed relative high and stable activity for the steam reforming of naphthalene and benzene at 1023-1073 K under steady state and in cyclic usage test[3]. Recently, our research group has been proposed a novel purification process for the impurities derived from steam gasification of woody biomass and just started to find out the material for selective H_2S decomposition and the catalyst for simultaneous decomposition of biomass tar and NH_3. In this process, simultaneous decomposition of tar and NH_3 should proceed at less than 923 K to prevent heat loss from gasification to this step. Although Ni-based catalysts are generally accepted as effective catalysts for tar removal, significant carbon deposition are likely happened over those catalysts, especially at low temperature. Thus, in this study, Ni/Al_2O_3 and Ba-Ni/Al_2O_3 catalysts were prepared and used for steam reforming of naphthalene/benzene at 923 K to discuss the effect of Ba addition on the catalytic performance.

2. Experimental

2.1 Catalyst preparation

Ni/Al_2O_3 catalysts were prepared by the conventional impregnation method. The prepared Ni/Al_2O_3 catalysts were dried at 383 K for 12 h and calcined at 873 K for 3 h. For Ba-Ni/Al_2O_3 catalyst, the calcined powder was added into $Ba(NO_3)_2$ aqueous solution with controlling Ba/Ni molar ratio of 0.25, and dried and calcined under same condition as mentioned. The catalysts before and after reaction were characterized by XRD, XRF, H_2-pulse chemical adsorption and TG-DTA.

2.2 Steam reforming of naphthalene/benzene

All prepared catalysts were tested in atmospheric flow reactor system. Calcined catalysts were reduced with H_2/He (50vol%/50vol%) mixed gas at 973 K for 2 h. After reduction, the reactor was cool down to 823~

923K, and the reactant mixture of naphthalene/benzene/H_2O/N_2/He (1/9/19/10/61 mol%) was passed through the catalyst bed. Non-reacted naphthalene/benzene and H_2O was trapped, and non-condensable gaseous products were analyzed by the GC-TCD. The catalytic activity in the steam reforming was evaluated by carbon conversion to gas [%] calculated using the equation described below:

Carbon conversion to gas [%] =

$$\{CO\ [ppm] + CO_2\ [ppm] + CH_4\ [ppm]\} / \{6\times C_6H_6\ [ppm] + 10\times C_{10}H_8\ [ppm]\}\times 100 \quad [1]$$

The amount of carbon deposited on the tested catalysts was analyzed by TG-DTA, and the effect of Ba addition on the amount of carbon deposition and catalytic activity in steam reforming was discussed.

3. Results and discussion

Figure 1 and **Figure 2** show the catalytic performances of Ni/Al_2O_3 and Ba-Ni/Al_2O_3 for the steam reforming of naphthalene/benzene at 923 K with S/C molar ratio of 3. It was seen that the Ba addition improved carbon conversion to gas and increased the concentrations of CO and H_2 during all reaction times. If considering the concentrations of CO_2, CH_4 and H_2 and H_2O conversion, the water gas shift reaction rate might be constant for both catalysts, whereas the steam reforming reaction rate was improved by Ba addition for Ni/Al_2O_3.

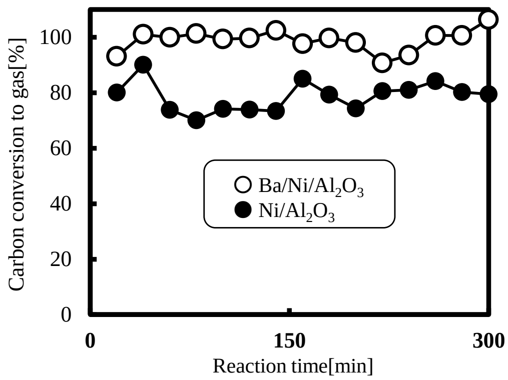

Figure 1 Carbon conversion to gas during the reaction at 923 K with S/C molar ratio of 3.

Table 1 shows amounts of carbon deposition in steam reforming at three temperatures (823~923 K) with similar carbon conversion to gas adjusted by changing GHSV (gas hourly space velocity). If the similar carbon conversion to gas was obtained for both catalysts, meaning that GHSV was different between them, a lower amount of carbon deposited on Ba-Ni/Al_2O_3 catalyst was obtained at all tested reaction temperatures. Moreover, an increase in CO concentration and a slight decrease in CO_2 concentration were observed for Ba-Ni/Al_2O_3 catalyst, indicating that the steam reforming reaction was promoted by Ba addition for Ni/Al_2O_3 catalyst.

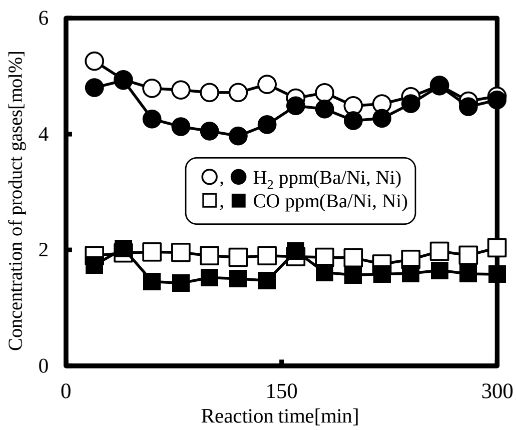

Figure 2 Concentration of product gases during the reaction at 923 K with S/C molar ratio of 3.

Table 1 The amount of carbon deposited during the reaction

Temp. [K]	Carbon Conv. [%]	Carbon deposited [mg g^{-1} h^{-1}] Ni/Al_2O_3	Ba-Ni/Al_2O_3
923	78	16.5	8.1
873	62	20.0	12.0
823	39	28.0	6.8

4. Conclusion

It was concluded from the obtained results that the Ba addition for Ni/Al_2O_3 catalyst promoted the steam reforming reaction rate and suppressed the amount of carbon deposited on the catalyst.

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