Steam Reforming of Toluene Over Ni/Coal Ash Catalysts: Effect of Coal Ash Composition

Jinyoung Jang*, Gunung Oh*, Ho Won Ra, Sung Min Yoon**, Tae Young Mun**, Myung Won Seo**,
Jihong Moon**, Jae-Goo Lee*,*** and Sang Jun Yoon**,†**

**Advanced Energy Technology, Korea University of Science and Technology,
217 Gajeong-ro, Yuseong-gu, Daejeon, 34113 Korea*
***Climate Change Research Division, Korea Institute of Energy Research,
152 Gajeong-ro, Yuseong-gu, Daejeon, 34129 Korea*
****Future Energy Plant Convergence Research Center, Korea Institute of Energy Research,
152 Gajeong-ro, Yuseong-gu, Daejeon, 34129 Korea*

Abstract. The development of a low cost catalyst with high performance and small amount of carbon deposition on catalyst from toluene steam reforming were investigated by using coal ash as a support material. Ni-loaded coal ash catalyst showed similar catalytic activity for toluene steam reforming compared with the Ni/Al$_2$O$_3$. At 800 $^\circ$C, the toluene conversion was 77% for Ni/TAL, 68% for Ni/KPU and 78% for Ni/Al$_2$O$_3$. Ni/TAL showed similar toluene conversion to Ni/Al$_2$O$_3$. However, Ni/KPU produced higher hydrogen yield at relatively lower toluene conversion. Ni/KPU catalyst showed a remarkable ability of suppressing the carbon deposition. The difference in coke deposition and hydrogen yield is due to the composition of KPU ash (Ca and Fe) which increase coke resistance and water gas shift reaction. This study suggests that coal ash catalysts have great potential for the application in the steam reforming of biomass tar.

Key words: Biomass tar, Toluene, Reforming, Coal ash, Coke resistance

1. Introduction

Biomass produces carbon neutral energy with diverse transformation technologies as renewable energy resources, which attracts a lot of attention [1-3]. Among biomass conversion technologies, gasification can generate syngas (synthesis gas) that mostly containing H$_2$ and CO and be used as electrical power generation (fuel cell, gas turbine or engine) and as feedstock for the synthesis of liquid fuels and various chemicals [3,4]. Despite these advantages, tar be produced through biomass gasification has a problem that it is adhered to pipes, engines, etc. of the gasification system to hinder process efficiency and syngas utilization [5].

Generally, the content of tar in the syngas covered varies from 1 to 100 g/Nm^3 depending on condition such as feedstock, type of gasifier, gasification agent, bed material and gasification temperature [6,7]. Syngas application device requires a very limited concentration of tar in syngas from 0.1 to 500 mg/Nm^3 [8]. Therefore, it is necessary to remove the tar to commercialize the biomass gasification technology. There are physical, thermal and catalytic methods for tar removal. The physical method has problems that it must be cool before the last separation and a large amount of wastewater is generated. Thermal method has a problem that the temperature must be increased to 1000 $^\circ$C. However, catalytic method has the advantages that tar can

be removed from low temperatures and fuel value is increases [9].

Up to now, biomass tar reforming using catalyst has been carried out through various experiments. Types of catalysts can be classified into nickel-based, non-nickel metal, alkali metal, basic, acid and activated carbon catalyst. Nickel-based catalysts, which are effective against cracking and reforming tar, are composed of active materials, promoters, and supports. Experiments have been carried out with a variety of promoters to enhance activity and stability, and supports to provide high surface area and carbon deposition resistance [5,10,11].

As another direction of research, many efforts have been made to use new materials that are not used as catalysts. The catalyst made with chicken droppings and chicken droppings ash showed good catalytic performance even at low temperatures to remove tar produced by biomass pyrolysis [12]. In a study to reforming of biomass tar by using alkaline properties and porous structure of scallop shells, they confirmed the catalytic potential for the scallop shell by loading metal oxide on the scallop shell [13].

The coal ash from the power plant has been landfilled or recycled (e.g. cement production) [14]. In the future, landfill sites will be scarce and increase disposal costs. Landfilled ash will be a source of serious environmental problems. Therefore, we must study various ways in which coal ash can be recycled. Commonly, coal ash contains a large amount of SiO$_2$ and Al$_2$O$_3$, which have large pore structure, thermal and structural stability characteristics of the catalyst support [15-18]. Further, the coal ash contains a metal oxide such as alkali metal and earth metal. These materials can be used as active materials in catalysts. The production of catalysts using coal ash is a method to utilize coal ash as high value [14,19]. That is, if coal ash is used in the

production of catalyst, it is possible to reduce the consumption of the catalyst materials and reduce the manufacturing cost [20].

In this study, biomass tar steam reforming was carried out using toluene as a biomass tar. Stable and highly active catalysts were prepared for low cost by using coal ash as a support and promoter. The coal ash used in the study was divided into coal ash containing many promoter components and coal ash containing a large amount of support materials. By doing so, the difference and effect of ash components between the two coal ashes can be identified and compared. Also, the carbon deposition resistance of coal ash catalysts under severe condition was studied. Toluene steam reforming performance was evaluated according to each experimental condition.

2. Experimental

2-1. Catalyst preparation

The coal ash used for the preparation of the catalysts is KPU (Indonesian sub-bituminous coal) ash and TALDINSKY (Russian sub-bituminous coal) ash. The composition of coal ash is as shown in Table 1. The catalysts used for the toluene steam reforming are listed in Table 2, Ni was loaded onto three kinds of supports such as α-Al_2O_3, TALDINSKY ash and KPU ash as an active material. The reason for the 12 wt% Ni content is that high conversion is shown at 10-20 wt%, and higher content of Ni leads to fast inactivity [21]. $Ni(NO_3) \cdot 6H_2O$ (JUNSEI, Extra pure) was used as a Ni precursor, and coal ash (TALDINSKY, KPU, 250 μm under) and α-Al_2O_3 (Alfa Aesar, 99.9%, 1 μm) were used as supports.

The catalysts were prepared by adding distilled water, $Ni(NO_3) \cdot 6H_2O$, a support (α-Al_2O_3, TALDINSKY ash, KPU ash) to the flask and stirring with stirrer at 70 $^\circ$C for one day. After that, catalysts were dried in oven at 105 $^\circ$C for one day, then calcined at 800 $^\circ$C for 3 hours in a furnace. The catalysts were pulverized and sieved to a size of 150~200 μm for use of the experiment.

### 2-2. Characterization of catalysts

The components and contents of coal ash were analyzed by using X-ray Fluorescence Spectrometer (XRF, Rigaku, ZSX Primus IV) to confirm the materials acting as a support and promoter for the catalysts. Specific surface area analyzer (TriStar II3020) was used to measure the specific surface area of the catalysts. X-ray Diffractometer (XRD, Rigaku, SmartLab) was used to observe the presence of Ni and crystal size of the catalysts. Thermogravimetric Analyzer (TGA, SCINCO, TGA N-1500) was used to determine the carbon deposition tendencies towards the catalysts used in the experiments.

Table 2. The composition of catalysts used in this study

Catalyst	Active material	Support
Ni/Al	Ni 12 wt%	α-Al_2O_3
Ni/TAL	Ni 12 wt%	TALDINSKY ash
Ni/KPU	Ni 12 wt%	KPU ash
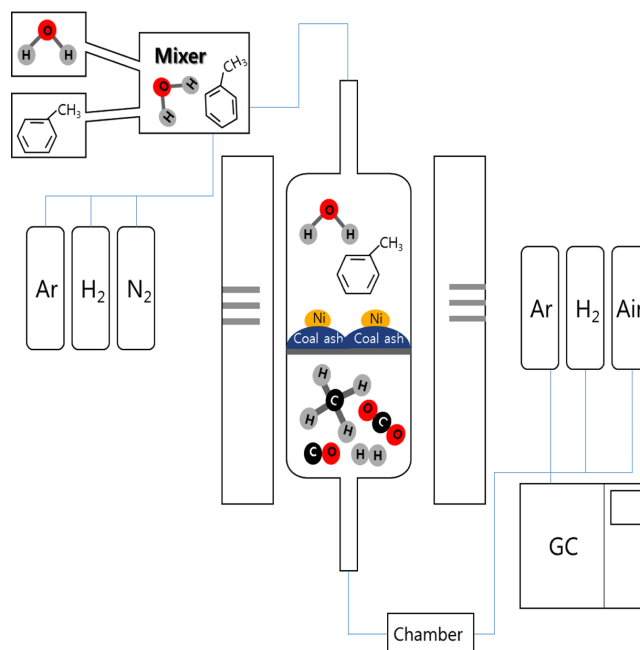
Fig. 1. Schematic diagram of catalytic toluene steam reforming system.

2-3. Procedure for toluene steam reforming

Fig. 1 shows a schematic diagram of the lab-scale tar reforming system used in this study. Toluene (30 g/Nm^3) and water vapor (Steam/Toluene molar ratio = S/T = 25) are supplied to the gas mixer uniformly using a syringe pump (kdscientific, legacy-200, legato-100). Water and toluene were vaporized by using a band heater. A mixture of water and toluene was introduced into a reactor through a gas mixer where it was contacted with nitrogen supplied from the mass flow controller (MFC, MKP, TSC-210). Inside the heater, a quartz tube having a diameter of 20 mm and a length of 570 mm was used as a reactor.

In order to minimize the mass transfer effect, a quartz bead was added and a preliminary experiment was conducted to determine the appropriate particle size and flow range [22]. The external diffusion effect was observed while increasing the flow rate and catalyst weight at fixed ratio. The internal diffusion effect was measured while increasing the catalyst particle size range. As a result, the mass transfer effect was negligible at a flow rate of 60 ml/min or more and a catalyst particle size of 200 μm or less.

Table 1. Composition of coal ash (wt%)

Coal ash	Ash composition (wt.%)										
	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	P_2O_5	MnO	SO_3
TALDINSKY ash	21.87	58.21	9.53	3.31	0.89	1.26	1.81	0.28	1.50	0.13	1.18
KPU ash	12.52	13.64	16.98	33.59	7.26	0.89	0.65	3.96	0.15	0.10	10.26

The amount of catalyst (about 0.1 g) was determined on the basis of a carrier gas flow rate of 60 ml/min, a catalyst particle size of 150 to 200 μm and a gas hourly space velocity (GHSV) of 50,000 h^{-1}, and a quartz bead were used together as a diluent. The catalyst was reduced with hydrogen and argon at a ratio of 1:1 before the experiment at 800 °C for 1 hour. The reduced catalyst and quartz bead in the reactor were maintained at the specified temperature using a furnace. Unreacted toluene and steam are collected in the chamber at the bottom of the reactor. The product gas was injected into gas chromatography (Agilent HP6890) and analyzed by thermal conductivity detector (TCD) and flame ionization detector (FID) through the column (porapak Q and CARBOSPHERE). Measurements were performed at least 5 times under the same conditions. The mean value were used to represent the results, and the standard deviation of the data were less than 5%. The flow rate of the product gas was calculated using the inert nitrogen gas analyzed in GC, and the molar flow rate (Vx) of each composition was calculated using the product gas flow rate. The conversion of toluene was calculated using the following Eq. (1).

$$Xc = \frac{V_{CO} + V_{CO_2} + V_{CH_4}}{V_{C_7H_8} \times 7} \times 100\% \tag{1}$$

3. Results and discussion

3-1. Characteristic of Ni-loaded catalysts and coal ash

The XRD patterns of the two kind of coal ash and Ni loaded catalysts after reduced at 800 °C for 1 hour are shown in Fig. 2. The peaks of Ni were found at $2\theta = 44°$, $52°$ and $76°$ in Fig. 2(c), (d) and (e). The Ni crystal sizes are calculated by the Scherrer equation. Ni crystal size of Ni/KPU shows larger than Ni/TAL and Ni/Al (Ni/KPU :
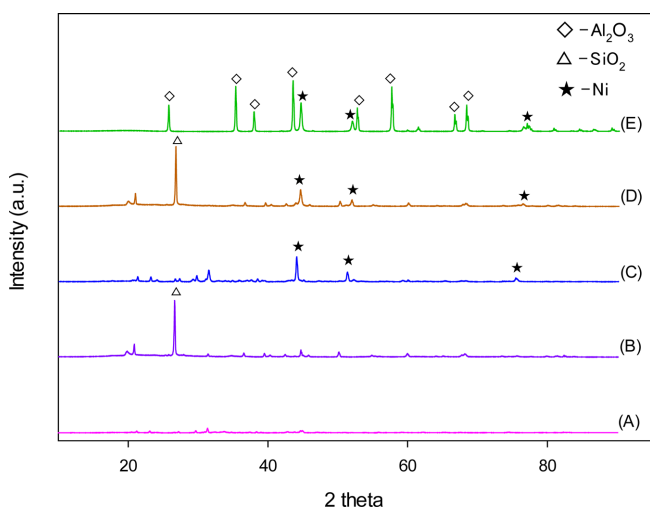

Fig. 2. XRD patterns of coal ashes and catalysts: (a) KPU ash, (b) TALDINSKY ash, (c) Ni/KPU, (d) Ni/TAL, (e) Ni/Al.
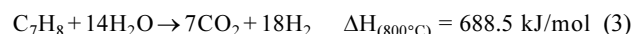
46.7 nm > Ni/Al : 39.5 nm > Ni/TAL : 34.5 nm). The large crystal size of Ni means that the specific surface area of the active material of the catalyst is relatively small. This difference in Ni crystal size is thought to be due to the large amount of Ca contained in Ni/KPU occupying the surface of the support and interfering with the interaction between Ni and Al_2O_3 [23].

The specific surface area of the supports (coal ashes and Al_2O_3) and catalysts are shown in Table 3. For the measurement of the specific surface area which satisfied the experimental conditions of toluene steam reforming, supports and catalysts were reduced in H$_2$ atmosphere at 800 °C for 1 hour. As a result, it was found that the specific surface areas of the supports and catalysts used in the experiment were generally small. It was found that TALDINSKY ash and Ni/TAL had the widest specific surface area when compared to other supports and catalysts before and after Ni loading.
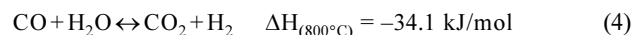
3-2. Toluene steam reforming over coal ash catalysts

Toluene steam reforming takes place through a comprehensively various reactions. The following equations are typical chemical reactions that occur during the toluene steam reforming.

Toluene steam reforming

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \quad \Delta H_{(800°C)} = 927.2 \text{ kJ/mol} \tag{2}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \quad \Delta H_{(800°C)} = 688.5 \text{ kJ/mol} \tag{3}$$

Water gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{(800°C)} = -34.1 \text{ kJ/mol} \tag{4}$$

When three kinds of catalysts were used under a constant conditions of S/T molar ratio 25, GHSV 50,000 h^{-1}, toluene steam reforming was performed according to the reaction temperature. The toluene conversion as a result of toluene steam reforming is shown in the Fig. 3. Based on the comparison of the toluene conversion with Ni/Al, which is widely used for hydrocarbon reforming, coal ash catalysts (Ni/TAL and Ni/KPU) showed similar or slightly lower value. As the temperature increased, the toluene conversion was also increased. Ni/Al and coal ash catalysts did not show much difference and showed a similar tendency.

In the Table 3, Ni/TAL was expected to have an effect on toluene steam reforming because it has a larger specific surface area than other catalyst. However, toluene steam reforming results in Fig. 3 showed that the specific surface area of catalyst does not have a large effect [10].

The dispersion of Ni is also related to catalytic activity. The smaller the size of the Ni particles, the better the dispersion on the support [23]. Due to the large Ni crystal size and low dispersion (Fig. 2), toluene steam reforming using Ni/KPU catalyst was generally considered to be

Table 3. BET surface area of supports and catalysts

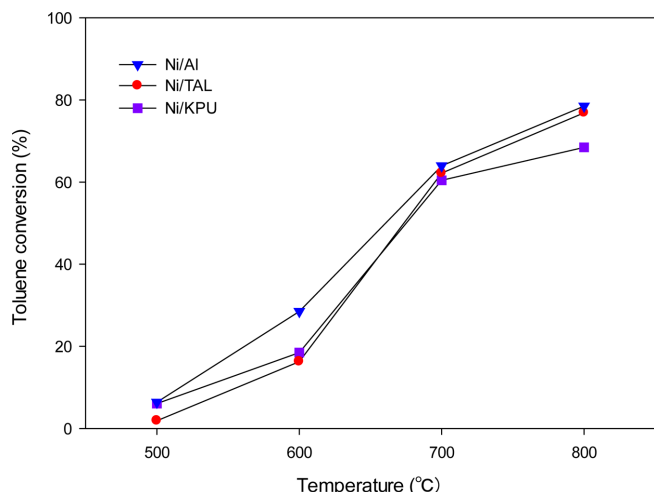| Support and catalysts	KPU ash	TALDINSKY ash	*α-Al$_2$O$_3$	Ni/KPU	Ni/TAL	Ni/Al
BET surface area (m^2/g)	5.4	9.5	6-8	3.2	10.1	5.3

*Alfa Aesar

Fig. 3. Effect of temperature on toluene conversion (S/T molar ratio: 25, GHSV: 50,000 h^{-1}).

less active than other catalysts throughout the experimental temperature.

The product gas composition after toluene steam reforming according to the reaction temperature is shown in Fig. 4. In common, CH_4 was hardly produced in all three catalysts, and the amounts of H_2 and CO increased as the temperature raised. However, the amount of product gases of Ni/TAL catalysts was different from other catalysts. The toluene conversion of Ni/TAL was similar to that of Ni/Al, but the reason for the less H_2 and CO_2 in Ni/TAL is that the water gas shift reaction (eq. 4) was less due to the large SiO_2 content of TALDINSKY ash. Water adsorption of Al_2O_3 is better than SiO_2, and water gas shift reaction in Al_2O_3 is more easily caused by water adsorption influence [24]. H_2/CO ratio in the gas produced by using Ni/TAL catalyst showed 2.19 which was lower than other catalysts. However, this H_2/CO ratio is close to 2.15, which can be used directly in the Fischer-Tropsch synthesis process [25].

The toluene conversion of Ni/KPU was 68% at 800 °C, which was lower than the other two catalysts (Ni/Al = 78%, Ni/TAL = 77%), but showed a high H_2/CO ratio 4.03 (Ni/Al = 3.98 and Ni/TAL = 2.19). The reason why Ni/KPU had a low toluene conversion but a large amount of hydrogen in the product gas was because Fe occupied about 17 wt% of KPU ash and promoted water gas shift reaction (eq. 4) to increase H_2 and CO_2 production [26,27].

3-3. Coke resistance of catalysts

Fig. 5 shows changes in the toluene conversion for 14 hours after reaching a stable condition at 700 °C under a low steam to toluene molar ratio (S/T = 1.4) which is a severe condition for stability of the catalyst. Ni/Al maintained the toluene conversion in the range of 53~55% and decreased after 11 hours. In the case of Ni/TAL, the toluene conversion was maintained at about 40% and showed slowly decreased. By contrast, Ni/KPU maintained the toluene conversion to 40% and increased slightly after 11 hours.
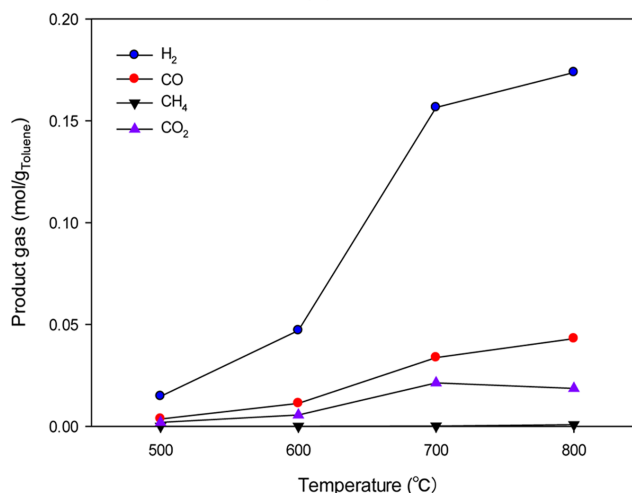
To investigate the relation between the results of the toluene steam reforming and coke deposition, the amount of coke deposition and
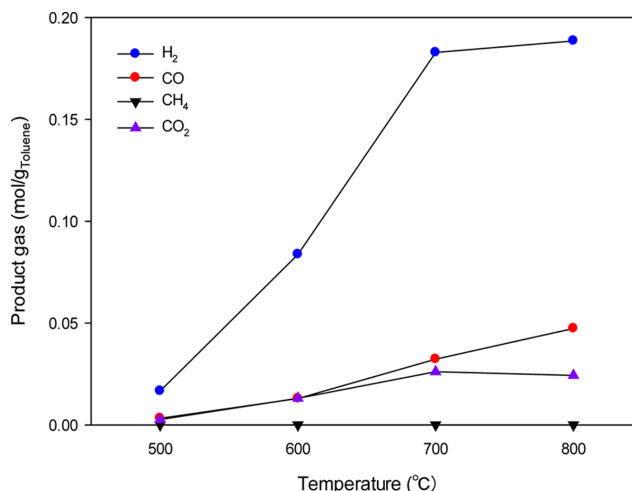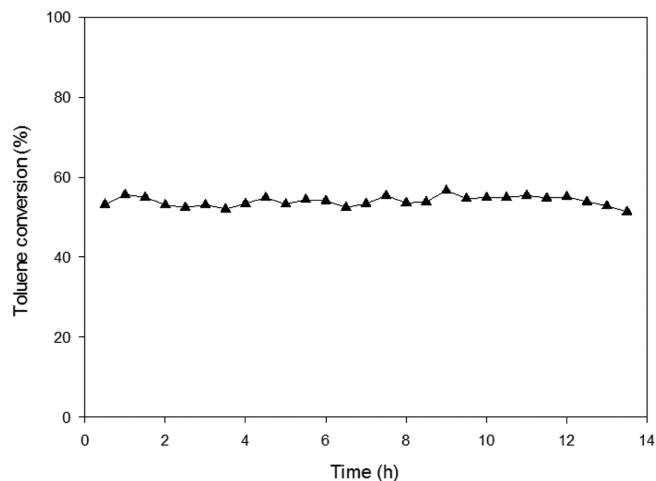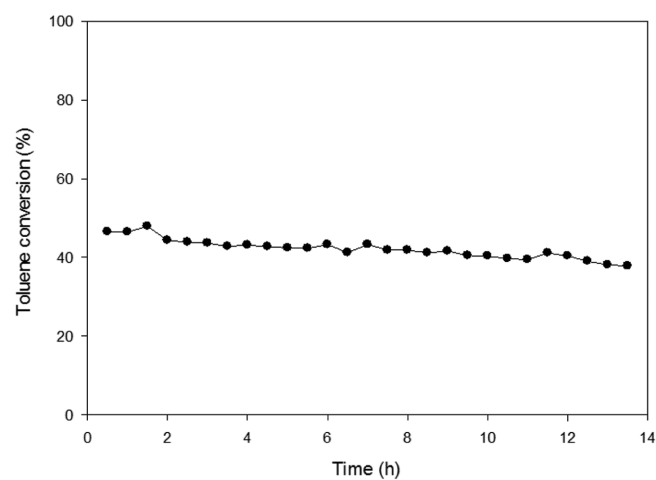

(a) Ni/Al
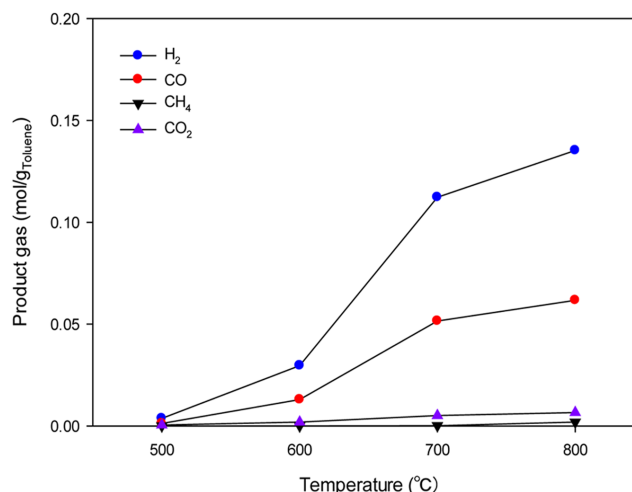
(b) Ni/TAL

(c) Ni/KPU

Fig. 4. Variation of product gas composition with temperature (S/T molar ratio: 25, GHSV: 50,000 h^{-1}).
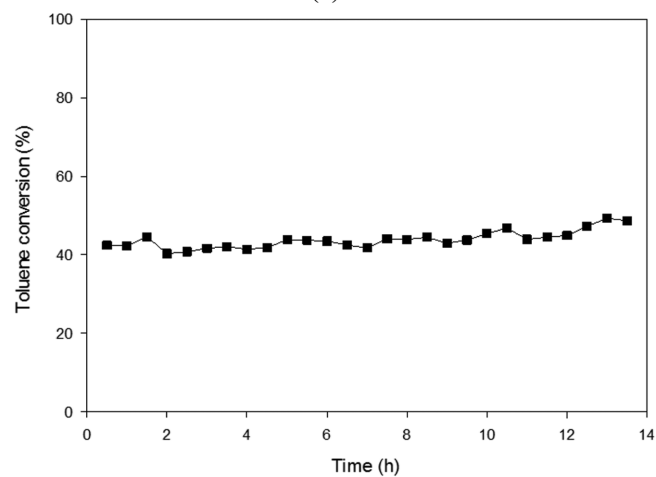
tendency were examined by TG analysis. Weight changes of the reduced fresh catalysts (800 °C, H_2, 1 hour) and used catalysts (Fig. 5
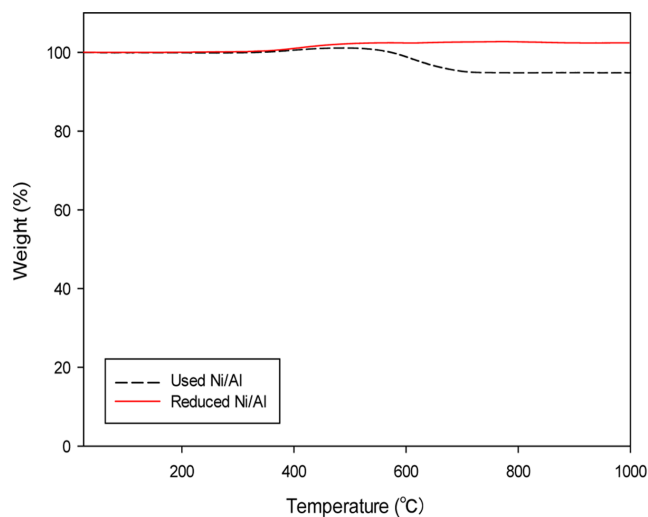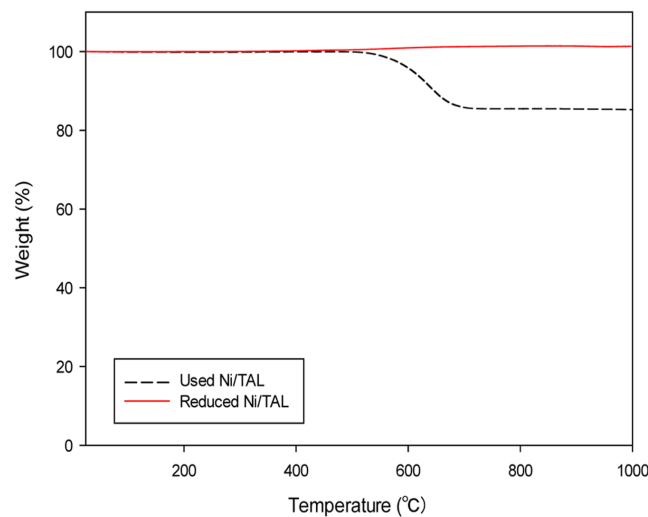
(a) Ni/Al

(b) Ni/TAL

(c) Ni/KPU

Fig. 5. Catalytic stability after steady state at 700 ℃, S/T molar ratio of 1.4.

(a) Ni/Al

(b) Ni/TAL

(c) Ni/KPU

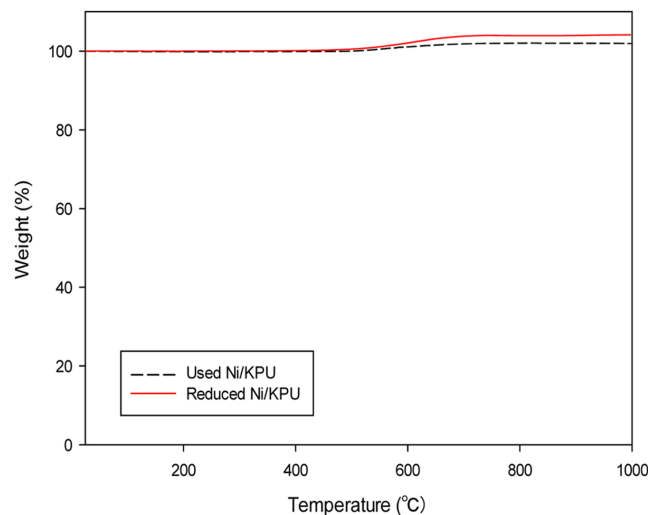**Fig. 6. TG analysis results of used and reduced (a) Ni/Al, (b) Ni/TAL, and (c) Ni/KPU catalyst.**

catalysts) were measured up to 1000 ℃ in the air condition. TG analysis results according to the reaction temperature were shown in Fig. 6. From the result, used Ni/TAL and Ni/Al catalyst showed a decrease in weight because of the combustion of deposited coke in the catalyst (Fig. 6(a), (b)). On the contrary, used Ni/KPU catalyst

shows an increase in weight due to the oxidation of Ni (Ni $\rightarrow$ NiO), which was larger than coke combustion (Fig. 6(c)).

In Fig. 6, the amount of coke deposition was calculated from the difference in the weight loss after the oxidation reaction between the reduced fresh catalyst and the used catalyst. As a result, coke deposition was occurred 34.6 $mg/g_{catalyst}$ in Ni/Al, 79.6 $mg/g_{catalyst}$ in Ni/TAL, 9.8 $mg/g_{catalyst}$ in Ni/KPU. Since the toluene conversion is different from each catalyst, a numerical value is required that can accurately compare the amount of carbon deposition. Therefore, when calculating the coke deposition amount per toluene conversion, Ni/Al can be calculate as 0.67, Ni/TAL as 1.99, and Ni/KPU as 0.25. Both of the results confirm that Ni/KPU showed the least accumulation of coke. The reason why Ni/KPU had the lowest coke deposition is that KPU ash has a large amount of Fe and Ca. Fe suppresses coke deposition and improves the stability of steam reforming reactions [28]. Moreover, the acidity of the support is neutralized by CaO to suppress cracking and polymerization reactions thereby promoting the reaction between water vapor and coke and inhibiting coke deposition [29].

CO_2 activation plays an important role in inhibition of coke deposition which involves coke and carbon dioxide reaction. Al_2O_3 can activate CO_2 while SiO_2 cannot activate CO_2. As a result, when Ni/SiO_2 catalyst is used, a problem of accumulation of coke occurs [30]. Therefore, it is thought that the high content of SiO_2 in TALDISKY ash is the reason why many coke deposits occurred in the Ni/TAL catalyst.

After the toluene reforming under severe condition (Fig. 5), the amount of coke deposition on Ni/TAL was more than twice that of Ni/Al, but Ni/TAL catalyst showed little deactivation characteristics. As shown in Fig. 6(b), weight loss occurred around 600 °C, which means that the filamentous carbon was formed on the Ni/TAL catalyst. Coke is divided into amorphous carbon and filamentous carbon depending on the coke combustion temperature. Amorphous carbon begins to oxidize at 400~500 °C and filamentous carbon around 600 °C [28]. Filamentous carbon has less effect on catalytic activity than amorphous carbon [31,32]. For this reason, Ni/TAL catalyst are considered to have not shown rapid deactivation despite many coke deposits.

4. Conclusion

The effect of two kinds of coal ash (TALDINSKY ash and KPU ash) catalysts on toluene steam reforming was investigated. In the case of a catalyst using KPU ash containing a high content of Ca and Fe, the coke deposition resistance was enhanced during toluene steam reforming under the severe condition (S/T = 1.4, GHSV = 50,000h^{-1}), and showed high H_2/CO ratio in the product gas due to enhanced the water gas shift reaction. TALDINSKY ash catalyst showed similar toluene conversion to Ni/Al at the overall reaction temperature. TALDINSKY ash occupied a large proportion of SiO_2, so under severe condition and long-term usage, Ni/TAL catalyst generates more coke deposits than the remaining two catalysts. Ni/TAL produced coke deposition twice as much as Ni/Al, but filamentous carbon accumulated on Ni/TAL did not cause the catalyst inactivity rapidly.

Finally, coal ash catalysts used in this study were found to be similar or better than Ni/Al in catalytic activity and coke resistance. Above all, coal ash can be used at a high value by using as a catalyst instead of landfill or low value utilization. It was confirmed that coal ash catalysts can reduce catalyst production cost by about 91% compared to Ni/Al used as a comparative catalyst. Coal ash catalyst has advantages and disadvantages depending on the composition of the coal ash. Therefore, it is possible that coal ash can be utilized as promoter as well as support according to the desired performance by using various coal ash components.

Acknowledgments

References

1. Cao, J. P., Liu, T. L., Ren, J., Zhao, X. Y., Wu, Y., Wang, J. X., Ren, X. Y. and Wei, X. Y., "Preparation and Characterization of Nickel Loaded on Resin Char as Tar Reforming Catalyst for Biomass Gasification," *J. Anal. Appl. Pyrol.*, **127**, 82-90(2017).

2. Setyawan, D., Yoo, J. H., Kim, S. D., Choi, H. K., Rhim, Y. J., Lim, J. H., Lee, S. H. and Chun, D. H., "Torrefaction Effect on the Grindability Properties of Several Torrefied Biomasses," *Korean J. Chem. Eng.*, **56**, 547-554(2018).

3. Han, S. W., Seo, M. W., Park, S. J., Son, S. H., Yoon, S. J., Ra, H. W., Mun, T.-Y., Moon, J. H., Yoon, S. M., Kim, J. H., Lee, U. D., Jeong, S. H., Yang, C. W. and Rhee, Y. W., "Air Gasification Characteristics of Unused Woody Biomass in a Lab-scale Bubbling Fluidized Bed Gasifier," *Korean J. Chem. Eng.*, **57**, 874-882(2019).

4. Guan, G., Kaewpanha, M., Hao, X. and Abudula, A., "Catalytic Steam Reforming of Biomass Tar: Prospects and Challenges," *Renewable Sustainable Energy Rev.*, **58**, 450-461(2016).

5. Anis, S. and Zainal, Z. A., "Tar Reduction in Biomass Producer Gas via Mechanical, Catalytic and Thermal Methods: A Review," *Renewable and Sustainable Energy Rev.*, **15**, 2355-2377(2011).

6. Oh, G., Park, S. Y., Seo, M. W., Ra, H. W., Mun, T. Y., Lee, J. G. and Yoon, S. J., "Combined Steam-Dry Reforming of Toluene in Syngas over CaNiRu/Al$_2$O$_3$ Catalysts," *Int. J. Green Energy*, **16**, 333-349(2019).

7. Oh, G., Park, S. Y., Seo, M. W., Kim, Y. K., Ra, H. W., Lee, J. G. and Yoon, S. J., "Ni/Ru-Mn/Al$_2$O$_3$ Catalysts for Steam Reforming of Toluene as Model Biomass Tar," *Renew. Energy*, **86**, 841-847 (2016).

8. Rios, M. L. V., González, A. M., Lora, E. E. S. and del Olmo, O. A. A., "Reduction of Tar Generated during Biomass Gasification: A Review," *Biomass Bioenergy*, **108**, 345-370(2018).

9. Schmidt, S., Giesa, S., Drochner, A. and Vogel, H., "Catalytic Tar Removal from Bio Syngas-Catalyst Development and Kinetic

Studies," *Catal. Today*, **175**, 442-449(2011).

10. Heo, D. H., Lee, R., Hwang, J. H., Sohn, J. M., "The Effect of Addition of Ca, K and Mn over Ni-based Catalyst on Steam Reforming of Toluene as Model Tar Compound," *Catal. Today*, **265**, 95-102(2016).

11. Quitete, C. P. B., Bittencourt, R. C. P. and Souza, M. M. V. M., "Steam Reforming of Tar Model Compounds over Nickel Catalysts Supported on Barium Hexaaluminate," *Catal. Lett.*, **145**, 541-548(2015).

12. Kannari, N., Oyama, Y. and Takarada, T., "Catalytic Decomposition of Tar Derived from Biomass Pyrolysis using Ni-loaded Chicken Dropping Catalysts," *Int. J. Hydrogen Energy*, **42**, 9611-9618(2017).

13. Guan, G., Chen, G., Kasai, Y., Lim, E. W. C., Hao, X., Kaewpanha, M., A. Fushimi, A. C. and Tsutsumi, A., "Catalytic Steam Reforming of Biomass Tar over Iron- or Nickel-based Catalyst Supported on Calcined Scallop Shell," *Appl. Catal. B-Environ.*, **115-116**, 159-168(2012).

14. Balakrishnan, M., Batra, V. S., Hargreaves, J. S. J. and Pulford, I. D., "Waste Materials – Catalytic Opportunities: an Overview of the Application of Large Scale Waste Materials as Resources for Catalytic Applications," *Green Chem.*, **13**, 16-24(2011).

15. Bepari, S., Pradhan, N. C. and Dalai, A. K., "Selective Production of Hydrogen by Steam Reforming of Glycerol over Ni/Fly Ash Catalyst," *Catal. Today*, **291**, 36-46(2017).

16. Ashok, J., Kathiraser, Y., Ang, M. L. and Kawi, S., "Ni and/or Ni-Cu Alloys Supported over SiO_2 Catalysts Synthesized via Phyllosilicate Structures for Steam Reforming of Biomass Tar Reduction," *Catal. Sci. Technol.*, **5**, 4398-4409(2015).

17. Lee, H. J., Kim, W. Lee, K. and Yoon, W. L., "Kinetic Model of Steam-Methane Reforming Reactions over Ni-Based Catalyst," *Korean Chem. Eng. Res.*, **56**, 914-920(2018).

18. Lee, S.-H., Lim, H., Kim, S. D. and Jeon, C.-H., "A Study on Ash Fusibility Temperature of Domestic Thermal Coal Implementing Thermo-Mechanical Analysis," *Korean Chem. Eng. Res.*, **52**, 233-239(2014).

19. Herman, A. P., Yusup, S. and Shahbaz, M., "Utilization of Bottom Ash as Catalyst in Biomass Steam Gasification for Hydrogen and Syngas Production," *Chem. Eng. Trans.*, **52**, 1249-1254(2016).

20. Blissett, R. S. and Rowson, N. A., "A Review of the Multi-component Utilization of Coal Fly Ash," *Fuel*, **97**, 1-23(2012).

21. Artetxe, M., Alvarez, J., Nahil, M. A., Olazar, M. and Williams, P. T., "Steam Reforming of Different Biomass Tar Model Compounds over Ni/Al_2O_3 Catalysts," *Energy Convers. Manage.*, **136**, 119-126(2017).

22. Swierczynski, D., Courson, C. and Kiennemann, A., "Study of

Steam Reforming of Toluene Used as Model Compound of Tar Produced by Biomass Gasification," *Chem. Eng. Process.*, **47**, 508-513(2008).

23. Dieuzeide, M. L., Laborde, M., Amadeo, N., Cannilla, C. and Bonura, G., "Hydrogen Production by Glycerol Steam Reforming: How Mg Doping Affects the Catalytic Behavior of Ni/Al_2O_3 Catalysts," *Int. J. Hydrogen Energy*, **41**, 157-166(2016).

24. Do, J. Y., Kwak, B. S., Park, N. K., Lee, T. J., Lee, S. T., Jo, S. W., Cha, M. W., Jeon, M. K. and Kang, M., "Effect of Acidity on the Performance of a Ni-based Catalyst for Hydrogen Production through Propane Steam Reforming: $K-AlSi_xO_y$ Support with Different Si/Al Ratios," *Int. J. Hydrogen Energy*, **42**, 22687-22697(2017).

25. Pala, L. P. R., Wang, Q., Kolb, G. and Hessel, V., "Steam Gasification of Biomass with Subsequent Syngas Adjustment Using Shift Reaction for Syngas Production: An Aspen Plus Model," *Renew. Energy*, **101**, 484-492(2017).

26. Zamboni, I., Courson, C. and Kiennemann, A., "Fe-Ca Interactions in Fe-based/CaO Catalyst/Sorbent for CO_2 Sorption and Hydrogen Production from Toluene Steam Reforming," *Appl. Catal. B-Environ.*, **203**, 154-165(2017).

27. Adnan, M. A., Muraza, O., Razzak, S. A., Hossain, M. M. and de Lasa, H. I., "Iron Oxide over Silica-Doped Alumina Catalyst for Catalytic Steam Reforming of Toluene as a Surrogate Tar Biomass Species," *Energy Fuels*, **31**, 7471-7481(2017).

28. Ahmed, T., Xiu, S., Wang, L. and Shahbazi, A., "Investigation of Ni/Fe/Mg Zeolite-Supported Catalysts in Steam Reforming of Tar Using Simulated-Toluene as Model Compound," *Fuel*, **211**, 566-571(2018).

29. Ashok, J. and Kawi, S., "Steam Reforming of Biomass Tar Model Compound at Relatively Low Steam-to Carbon Condition over CaO-doped Nickel-Iron Alloy Supported over Iron-Alumina Catalysts," *Appl. Catal. A-Gen.*, **490**, 24-35(2015).

30. Rodemerck, U., Scheider, M. and Linke, D., "Improved Stability of Ni/SiO_2 Catalysts in CO_2 and Steam Reforming of Methane by Preparation via a Polymer-Assisted Route," *Catal. Commun.*, **102**, 98-102(2017).

31. Josuinkas, F. M., Quitete, C. P. B., Ribeiro, N. F. P. and Souza, M. M. V. M., "Steam Reforming of Model Gasification Tar Compounds over Nickel Catalysts Prepared from Hydrotalcite Precursors," *Fuel Process. Technol.*, **121**, 76-82(2014).

32. Park, S. Y., Oh, G., Kim, K., Seo, M. W., Ra, H. W., Mun, T. Y., Lee, J. G. and Yoon, S. J., "Deactivation Characteristics of Ni and Ru Catalysts in Tar Steam Reforming," *Renew. Energy*, **105**, 76-83(2017).