Catalytic properties of Rh/CeO$_2$/SiO$_2$ for synthesis gas production from biomass by catalytic partial oxidation of tar

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Abstract

Performance of Rh/CeO$_2$/SiO$_2$ in the partial oxidation of tar from the pyrolysis of wood biomass (architectural salvage) was investigated and compared with various materials such as steam reforming Ni catalyst, active clay, USY zeolite, MS-13X, dolomite, alumina, silica sand, fluorspar and non-catalyst. Rh/CeO$_2$/SiO$_2$ and the steam reforming Ni catalyst exhibited much higher performance than any other materials in terms of hydrogen production and the amount of tar. Therefore, the performance of Rh/CeO$_2$/SiO$_2$ and steam reforming Ni catalyst was particularly compared. From the result on the dependence of reaction temperature, equivalence ratio, and biomass feeding rate, Rh/CeO$_2$/SiO$_2$ exhibited higher performance than the Ni catalyst, especially in terms of tar and coke amount. Furthermore, Rh/CeO$_2$/SiO$_2$ was also more stable than the Ni catalyst. The catalyst deactivation can be related to the amount of coke deposition. The results indicate that Rh/CeO$_2$/SiO$_2$ has high resistance to coke formation, and this is related to higher combustion activity of Rh/CeO$_2$/SiO$_2$ than the Ni catalyst. Furthermore, from the TPR profiles, Rh/CeO$_2$/SiO$_2$ had higher reducibility than the Ni catalyst. The combination of high combustion activity with high reducibility and reforming activity can be related to high performance of tar conversion in the fluidized bed reactor.

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1. Introduction

Biomass, an abundantly available and renewable energy resource, has been considered either as a combustion fuel for power generation or as a waste, causing disposal problems. However, the syngas production from the tar derived from biomass offers substantial advantages from the point of view of environmental protection and CO$_2$ emission. This is because the synthesis gas can be converted to clean fuels, which contribute significantly to the reduction of the net CO$_2$ emission into the atmosphere. Fischer–Tropsch synthesis gives clean diesel fuel. Dimethyl ether, which is a promising super-clean fuel in the future, can be produced with high efficiency from the synthesis gas. Thus, a growing interest in this field has been drawn recently to discover more efficient process for biomass gasification [1–8].

The conventional gasification of biomass has many drawbacks: it is a very high-temperature process (1123–1323 K) and gives many byproducts such as tar, char, ammonia and sulfur compounds with the product gases such as H$_2$, CO, CO$_2$, H$_2$O and light hydrocarbons [9–11]. The use of product gases in advanced applications is hindered by the presence of these contaminants. Char can be separated by simple filtration method however; the tar is volatile and very difficult to condense even at cryogenic conditions and always remains in the gas stream, causing severe damage of engine parts and the catalyst in the subsequent catalytic conversion of product gas to liquid fuels and chemicals. The thermal conversion of biomass is a function of temperature, and the lower the temperature the higher the tar formation [12]. On the other hand, the low-temperature gasification process can be more energy-efficient. However, the low-temperature thermochemical conversion of biomass requires some secondary activators such as a catalyst for the removal of large amount of tar.

The use of catalysts in the biomass gasification system is the most effective approach in order to reduce the tar content in the product gas as well as to improve the product gas composition [13]. The performance of the catalysts in
the gasification processes depends on the utilization method of catalysts such as primary or secondary bed, and fluidized or fixed bed. Various kinds of catalysts such as nickel-based catalysts, olivine, oxides, dolomites, and zeolites have been widely investigated in different gasification systems [14]. Nickel-based catalysts were used in the steam reforming of condensable vapors derived from pyrolysis of biomass to produce hydrogen and synthesis gas [15–17]. It is pointed out that the problem in the catalytic process is the catalyst deactivation caused by the deposited coke on the catalyst surface [18–20]. Therefore, various additives have been attempted, and in some cases, the additive can decrease the coke formation, and make the catalyst life longer [21,22]. Dolomites have been also used for the decrease of tar reforming. However, the tar yield on the dolomite was much higher than that on nickel-based catalysts [23,24]. Recently, we have developed Rh/CeO₂/SiO₂ catalyst for the low-temperature gasification with air and/or steam using cellulose and cedar wood [25–31]. In this article, we investigate the performance in partial oxidation of tar derived from the pyrolysis of woods supplied from the architectural salvage using the dual-bed reactor.

In addition, the steam reforming of tar is highly endothermic reaction, and the external heating is required. However, in terms of energy efficiency of the systems, the internal heating is more suitable than the external heating. Catalytic partial oxidation of tar is one of the most promising methods of tar conversion to gaseous products even at low temperature. In this reaction, oxygen is introduced to the catalyst bed together with tar. The feeding amount of oxygen can be adjusted to auto-thermal condition, in this case, the external heating is not necessary. However, in the catalytic partial oxidation, the hot spot formation on the catalyst surface can be another problem. One of the methods to inhibit the hot spot formation is the utilization of fluidized bed reactor [32–34]. The hot spot is usually formed at the catalyst bed inlet because of high oxygen concentration. In the fluidized bed reactor, the catalyst particles are always moving, and this promotes the heat transfer, and gives homogenous bed temperature. Hot spot formation can be inhibited by this mechanism.

In this article, we carried out the activity test of various catalysts, especially Rh/CeO₂/SiO₂ and the steam reforming Ni catalyst in partial oxidation of tar, and we used the tar derived from the pyrolysis of wood biomass (architectural salvage), which is one of the promising biomass sources.

2. Experimental

2.1. Catalyst

In this article, we have tested various materials described below. Dolomite (21.0 mass% MgO, 30.0 mass% CaO, 0.7 mass% SiO₂, 0.1 mass% Fe₂O₃, and 0.5 mass% Al₂O₃), USY zeolite (Toasoh, SiO₂/Al₂O₃ = 14), molecular sieve 13X (denoted as MS-13X), fluorspar (CaF₂), alumina (Al₂O₃), active clay (SiO₂–Al₂O₃), silica sand (SiO₂), and steam reforming Ni catalyst. The Ni catalyst (ISOP, supplied from Sud-Chemie Catalysts Japan, Inc.) was used after crushed and sieved (0.08–0.35 mm). The composition was 12 mass% Ni and 88 mass% Al₂O₃. We also tested homemade Rh/CeO₂/SiO₂ catalyst, and the preparation method is as below. The CeO₂/SiO₂ support was prepared using granule SiO₂ (CARiACT G-6, size 0.18–0.50 mm, BET = 535 m²/g) supplied from Fuji Silysia Chemical Ltd. The CeO₂/SiO₂ was prepared by the incipient wetness method using the aqueous solution of Ce(NO₃)₃. After loading the Ce salt on SiO₂, it was dried at 383 K for 12 h following the calcination at 773 K for 3 h under air atmosphere. The loading of CeO₂ on SiO₂ was in the range of 30 mass%. Then the Rh was loaded on CeO₂/SiO₂ by impregnation of the support with acetone solution of Rh(C₅H₇O₂)₃. The loading amount of Rh was 1.2 mass%. After evaporating the acetone solvent, the catalyst was dried at 383 K for 12 h.

2.2. Biomass

Wood biomass was ground with a ball mill to about 0.1–0.3 mm size. The moisture content of the wood was about 9.6%. The dry-based composition was C 52.0 mass%, H 6.0 mass%, O 40.0 mass%, N 0.08 mass%, S 0.01 mass%, and ash 1.9 mass%. The elemental analysis was carried out by the Japan Institute of Energy.

Thermogravimetric analysis (TGA) of wood biomass was carried out by using DTA-60 (Shimadzu). Weight of the sample is about 10 mg. TGA was measured under the flowing air (20 ml/min) or N₂ (20 ml/min) and the heating rate was 15 K/min (300–1273 K).

2.3. Experimental apparatus and procedure

Activity tests of partial oxidation of tar (POT) derived from the pyrolysis of wood biomass were carried out in a laboratory-scale continuous feeding dual-bed reactor as shown in Fig. 1. This reactor contained the primary bed for pyrolysis of biomass and accumulation of solid products in pyrolysis reaction such as char and ash, and the secondary fluidized catalyst bed for POT. Tar is liquid at room temperature, and it is a mixture of various hydrocarbons and oxygenates, for example aromatics and carboxylic acid, according to our previous report [35]. However, at reaction temperature, tar can be vaporized. Therefore, tar can be introduced easily to the catalyst bed. The biomass feeder consisted of a conical glass vessel with a screw valve at the bottom, allowing continuous feeding of biomass particles by vibrating the vessel with an electric vibrator. Nitrogen was used for transporting the biomass particles to the primary bed.

This reactor had three ports for gas introduction and one port for the effluent gas. We chose gases from each port for
the evaluation of catalytic performance. In the evaluation of catalytic performance in POT, oxygen was introduced into the catalyst bed through the thin tube in the inner reactor (port A), and N\textsubscript{2} was also fed from the bottom of the outer reactor through a quartz distributor. In the estimation of yield of coke deposited on the catalyst, after the biomass feeding was stopped, oxygen (36 ml/min) was introduced from the port A, and N\textsubscript{2} (B: 50 ml/min and C: 100 ml/min) was fed from two other ports. Under this condition, coke combustion proceeds to form CO\textsubscript{2}. Coke amount can be estimated from the amount of CO\textsubscript{2}. Furthermore, in the estimation of char yield, the gas from port C was changed to O\textsubscript{2}/N\textsubscript{2} (36 C 100 ml/min), and N\textsubscript{2} (50 ml/min) was introduced from port B. The yield of solid char, which was formed in the pyrolysis of biomass and accumulated, was estimated from CO\textsubscript{2} formation on the basis of this procedure. The reaction temperature was controlled by the thermocouple outside the reactor as shown in Fig. 1. The tests were carried out under atmospheric pressure by using 1 or 3 g of a fresh catalyst. Before the test, the catalyst was pretreated under H\textsubscript{2} stream of 40 ml/min at 773 K for 0.5 h.

The effluent gas went through the filter and an iced water condenser so as to remove any solid and liquid materials, and it was collected by a syringe and analyzed by gas chromatograph (GC). The concentration of CO, CO\textsubscript{2}, CH\textsubscript{4} and C\textsubscript{2} (ethane and ethylene) was determined by FID-GC equipped with a methanator and that of H\textsubscript{2} was determined by TCD–GC. The flow rate of the gas was measured by a soap membrane meter. The carbon-based conversion to gas (C-conv.) was calculated by ‘A/B × 100’, where A represents the formation rate of CO+CO\textsubscript{2}+CH\textsubscript{4}+C\textsubscript{2} and B represents the total carbon supplying rate of biomass. In addition, the yield of carbon-containing gaseous products is also calculated by the ratio of the formation rate to the total carbon supplying rate of biomass. The yield of coke and char is calculated by (total amount of CO\textsubscript{2}+CO)/(total carbon amount in fed biomass). As a result, we can measure the yield of gaseous products and solid products (coke and char). However, it is difficult to determine the tar amount precisely. This is because tar is easily condensable in the reactor systems and a part of tar cannot be collected. Therefore, it is also difficult to determine the composition of tar, and we estimated the tar yield by subtraction of gaseous and solid product yields from the total. The yield of tar is defined as (100—C-conv. (%)—coke yield (%)—char yield (%)). The feeding rate of biomass, N\textsubscript{2}, and oxygen is described in each result. Equivalence ratio (ER) can be calculated by the ratio of feeding oxygen to oxygen for complete combustion of biomass.

2.4. Catalyst characterization

The methane combustion reaction was carried out on various catalysts within the temperature range of 523–1123 K using CH\textsubscript{4}/air Z 2/98 under atmospheric pressure. Catalyst weight was 0.09 g and W/F was 0.4 g h/mol.

Chemisorption experiments were carried out in high-vacuum system by volumetric methods. Research grade gas (H\textsubscript{2}: 99.99%, Takachiho Trading Co. Ltd) was used without further purification. Before H\textsubscript{2} adsorption measurement, the catalysts were treated in H\textsubscript{2} at 773 K for 0.5 h. H\textsubscript{2} adsorption was performed at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The sample
Fig. 3. Distribution of carbon containing products in the POT from wood biomass. Reaction conditions: wood biomass, 150 mg/min (H<sub>2</sub>O 9.6%, C, 5880 mol/min; H, 8140 mol/min; O, 3390 mol/min); O<sub>2</sub> 37 ml/min; N<sub>2</sub> 150 ml/min; catalyst 3 g, ER = 0.25, T = 823 K.

Table 1
Formation rate of products in the partial oxidation of tar from wood biomass

| Catalysts     | T (K)<sup>a</sup> | CO  | H<sub>2</sub> | CH<sub>4</sub> | C<sub>2</sub><sup>b</sup> | CO<sub>2</sub> |
|---------------|------------------|-----|-------------|-------------|-----------------|-------------|
|               | Formation rate (μmol/min) |     |             |             |                 |             |
| Rh/CeO<sub>2</sub>/SiO<sub>2</sub> | 823           | 1786 | 1436        | 412         | 44              | 1693        |
| 873           | 2427           | 2972 | 406         | 0           | 1640           |
| 923           | 2619           | 3571 | 290         | 0           | 1639           |
| Steam reforming | 823          | 1299 | 2056        | 269         | 30              | 2132        |
| Ni catalyst   | 873           | 1665 | 2541        | 325         | 46              | 2121        |
| 923           | 2332           | 3060 | 366         | 20          | 1751           |
| Active clay   | 823           | 986  | 144         | 367         | 33              | 1768        |
| 873           | 1416           | 220  | 422         | 37          | 2001           |
| 923           | 1624           | 342  | 500         | 49          | 2087           |
| USY zeolite   | 823           | 951  | 92          | 186         | 8               | 1690        |
| 873           | 1127           | 183  | 383         | 24          | 1837           |
| 923           | 1450           | 250  | 418         | 26          | 2011           |
| MS-13X        | 823           | 795  | 136         | 333         | 85              | 1998        |
| 873           | 1282           | 340  | 425         | 66          | 1574           |
| 923           | 1590           | 725  | 678         | 107         | 1694           |
| Fluorite      | 823           | 1114 | 119         | 347         | 19              | 1578        |
| 873           | 1346           | 171  | 388         | 35          | 1897           |
| 923           | 1693           | 260  | 475         | 0           | 2132           |
| Dolomite      | 823           | 810  | 120         | 184         | 2               | 1847        |
| 873           | 1301           | 146  | 313         | 52          | 1691           |
| 923           | 1538           | 186  | 404         | 68          | 1999           |
| Alumina       | 823           | 852  | 170         | 148         | 0               | 2097        |
| 873           | 1037           | 194  | 465         | 43          | 1732           |
| 923           | 1431           | 246  | 404         | 0           | 2283           |
| Silica sand   | 823           | 760  | 114         | 161         | 4               | 1759        |
| 873           | 1246           | 218  | 348         | 3           | 1765           |
| 923           | 1403           | 336  | 397         | 32          | 1987           |
| Non-catalyst  | 823           | 635  | 137         | 167         | 13              | 1751        |
| 873           | 1046           | 159  | 267         | 42          | 1868           |
| 923           | 1257           | 188  | 307         | 9           | 2096           |

Conditions: wood biomass, 150 mg/min (H<sub>2</sub>O 9.6%, C, 5880 mol/min; H, 8140 mol/min; O, 3390 mol/min); O<sub>2</sub> 37 ml/min; N<sub>2</sub> 150 ml/min; catalyst 3 g, ER = 0.25.

<sup>a</sup> Reaction temperature.
<sup>b</sup> C-basis.
weight was about 0.2 g. The dead volume of the apparatus was about 60 ml.

Temperature-programmed reduction (TPR) with H\textsubscript{2} was performed in fixed-bed flow reactor. The sample was pretreated in 100\% O\textsubscript{2} flow at 773 K for 1 h, and then it was cooled down to room temperature and exposed to helium flow in order to purge the line. The TPR profile of each sample was recorded from room temperature to 973 K under a flow of 5.0\% H\textsubscript{2}/Ar. The flow rate of 5.0\% H\textsubscript{2}/Ar was 30 ml/min, and the catalyst weight was 50 mg. The heating rate was 10 K/min and the temperature was maintained at 973 K for 10 min after it reached 973 K. The consumption of H\textsubscript{2} was monitored continuously with a TCD gas chromatograph equipped with frozen acetone trap in order to remove H\textsubscript{2}O from the effluent gas.

Transmission electron microscope (TEM) images were taken by means of JEM-2020F (JEOL) operated at 200 kV. Samples were dispersed in tetrachloromethane by supersonic waves and put on Cu grids for the TEM observation in the air.

3. Results and discussion

Fig. 2 shows thermogravimetric analysis (TGA) of wood biomass under N\textsubscript{2} and air flowing. Under N\textsubscript{2} flowing, the pyrolysis started at about 500 K, and rapid weight loss was observed in the range of 550–650 K, after this, slow pyrolysis was observed. Rapid part can be assigned to pyrolysis of cellulose and slow one can be due to pyrolysis of lignin. In our activity test, char is supplied from this slow pyrolysis part, and this behavior agrees with reaction temperature dependence of char amount as described later. In contrast, in the TGA profile under air flowing, the weight was decreased at a little lower temperature than that under N\textsubscript{2} flow. This is due to combustion reaction. Furthermore, the lignin combustion was also observed at 620–720 K. Since reaction temperature is higher than this lignin combustion temperature, it is found that it is possible to measure the amount of char by our method.

Fig. 3 shows the catalytic performance of various catalysts based on carbon yield in POT derived from the pyrolysis of wood biomass at 823–923 K, where the data were obtained for 15 min and catalyst weight was 3 g. The details of formation rate of the products are listed in Table 1. In the case of non-catalyst, coke was not observed at all, because coke is assigned to the carbon deposited on the catalyst surface. Without using catalysts, the tar yield was rather high, and formation rate of CO and H\textsubscript{2} was very small. On the other hand, the formation rate of CO\textsubscript{2} was very high, and this can be due to the combustion of tar with O\textsubscript{2}. The amount of char was almost the same in all the systems, and this is because the char is accumulated in the primary bed without the contact to the catalyst particles. In the case of the materials except the steam reforming Ni catalyst and Rh/CoO\textsubscript{2}/SiO\textsubscript{2}, the formation rate of H\textsubscript{2} was also the same level as that of non-catalyst. This indicates that catalytic partial oxidation of tar did not proceed. From the results, tar is converted to coke and CO without H\textsubscript{2} formation. On the other hand, in the case of Rh/CoO\textsubscript{2}/SiO\textsubscript{2} and steam reforming Ni catalyst, the tar amount decreased drastically, and the formation rate of H\textsubscript{2} and CO increased remarkably. This means that catalytic partial oxidation of tar can proceed over these catalysts.

Fig. 4 shows the relation between coke and tar yields over various catalyst. In the cases except Rh/CoO\textsubscript{2}/SiO\textsubscript{2}
and the steam reforming Ni catalyst, coke yield increased with decreasing tar yield. This can be because part of tar can be converted to coke. In contrast, Rh/CeO₂/SiO₂ and steam reforming Ni catalyst decreased tar amount drastically, however, coke amount was maintained to be small. This indicates that the tar is converted to other products than coke, and CO and H₂ was significantly increased from the result in Table 1. This can be explained by catalytic partial oxidation of tar. And these results support that Rh/CeO₂/SiO₂ and steam reforming Ni catalyst is very effective to the partial oxidation of tar to the synthesis gas.

Fig. 5 and Table 2 show the result of POT of tar using 1 g catalysts. In the results in Fig. 3 and Table 1, when 3 g catalyst was used, tar was not observed on both Rh/CeO₂/SiO₂ and the Ni catalyst. If the smaller amount of catalyst is used, it is possible to observe the tar yield more clearly. This is why the catalyst weight is decreased. Fig. 5 shows that tar yield on Rh/CeO₂/SiO₂ was much smaller than that on the Ni catalyst, and the difference was more significant at lower reaction temperature like 823 K. The formation rate of CO on Rh/CeO₂/SiO₂ was higher than that on the Ni catalyst at all reaction temperature as listed in Table 2. H₂ formation rate on Rh/CeO₂/SiO₂ was lower than Ni catalyst at 823 K. It should be noted that the coke yield on Rh/CeO₂/SiO₂ was also much lower than that of the Ni catalyst as shown in Fig. 5.

Fig. 6 shows effect of ER on the products distribution in the POT over Rh/CeO₂/SiO₂ and Ni catalyst at 873 K and ER = 0.25. Details of the formation rate of the products are listed in Table 3. In this experiment, ER is changed by adjusting oxygen flow rate. The formation rate of CO₂ increased and that of CO decreased with increasing ER. The formation rate of H₂ also increased with increasing ER, and this can be because the water gas shift reaction (CO + H₂O → CO₂ + H₂) is promoted by the increase of steam pressure. The steam is supplied in two ways. One is due to the pyrolysis of wood biomass, and the other is due to the reaction of introduced oxygen with tar and H₂. Even under high ER condition such as ER = 0.35, tar was not completely converted. On the other hand, no tar was observed on Rh/CeO₂/SiO₂ at ER = 0.25–0.35. In addition, coke amount on both catalysts was almost constant in the range of ER = 0.15–0.25. On the other hand, on both catalysts, coke amount became smaller at ER = 0.35 significantly. This suggests that the introduction of oxygen can play an important role in coke removal by the combustion.

Fig. 7 shows the effect of the biomass feeding rate in the POT over Rh/CeO₂/SiO₂ and Ni catalyst at 873 K and ER = 0.25. Details of the formation rate of the products are listed in Table 4. When the biomass feeding rate increased, C-conversion decreased, and tar and coke yields increased on both catalysts. It should be noted that the increase of coke amount with increasing biomass feeding rate over Rh/CeO₂/
SiO$_2$ was not as significant as that over the Ni catalyst. This indicates that Rh/CeO$_2$/SiO$_2$ has high resistance to coke formation during the reactions.

Although the activity test as shown above is based on the test for 15 min, the information on the catalyst life is also important. Therefore, we also carried out longer-time test. The result of the test at 873 K is represented in Fig. 8. Catalytic performance of Rh/CeO$_2$/SiO$_2$ decreased gradually for 40 min, however, in the range of 40–120 min, it was almost stable. In contrast, as shown in Fig. 8(b), the CO and H$_2$ formation rate over Ni catalyst decreased gradually even after 120 min. This can be due to the deactivation by deposited coke [36–38]. From the comparison at 120 min, Rh/CeO$_2$/SiO$_2$ showed much higher activity than the Ni catalyst. The amount of coke can be dependent on the rate of deposition and/or removal. Especially, when oxygen can be used, deposited carbon can be removed by the combustion reaction. This is expected by the TGA result (Fig. 2), and the previous reports also support this [32–34]. The removal rate can be dependent on the catalyst performance in combustion reaction. In order to evaluate the catalyst ability of combustion, we also carried out the activity test of methane combustion as a model reaction. Fig. 9 shows the reaction temperature dependence of methane combustion activity over Rh/CeO$_2$/SiO$_2$ and the Ni catalyst. On Rh/CeO$_2$/SiO$_2$, methane combustion started at about 500 K, in contrast, it started at about 700 K on the Ni catalyst. Especially in the case of the Ni catalyst, methane conversion cannot reach 100% at 1100 K. This result clearly shows the methane combustion activity of Rh/CeO$_2$/SiO$_2$ was much higher than that of Ni catalyst. This ability can be related to the high resistance to coke formation of Rh/CeO$_2$/SiO$_2$ in the partial oxidation of tar from wood biomass in the fluidized bed reactor.

Fig. 10 shows a model scheme of catalytic partial oxidation of tar from wood biomass in the fluidized bed reactor. Tar is introduced to the catalyst bed from the bottom of the catalyst bed, and the oxygen is introduced through a thin tube near the bottom of the catalyst bed. Since introduced amount of oxygen is far from the amount for total combustion of tar, oxygen is consumed in the lower part of the catalyst bed, and this part corresponds to oxidizing atmosphere. As reported previously, in this region, the combustion reaction can be catalyzed [26]. The coke amount can be influenced by the catalyst ability of combustion. On the other hand, since oxygen is consumed and absent, the upper part of the catalyst bed is in the reducing atmosphere, and CO + H$_2$ is present as the products. Therefore, the catalyst is reduced, and on the reduced catalysts, the steam reforming of tar can be catalyzed.

### Table 3

| Catalysts       | ER  | CO  | H$_2$ | CH$_4$ | C$_2$ | CO$_2$ | C-conv. (%) | Char (%) | Coke (%) | Tar (%) |
|-----------------|-----|-----|-------|--------|------|--------|-------------|----------|----------|---------|
| Rh/CeO$_2$/SiO$_2$ | 0.15 | 2395| 2599  | 419    | 32   | 1402   | 73.2        | 24.2     | 1.1      | 1.5     |
|                 | 0.25 | 2424| 2835  | 249    | 0    | 1814   | 76.7        | 22.3     | 1.0      | 0.0     |
|                 | 0.35 | 2098| 2910  | 85     | 0    | 2837   | 79          | 20.6     | 0.4      | 0.0     |
| Steam reforming | 0.15 | 1886| 1905  | 353    | 35   | 1537   | 65.8        | 23.2     | 3.9      | 7.1     |
| Ni catalyst     | 0.25 | 1761| 2463  | 215    | 75   | 1991   | 70.4        | 24.9     | 3.5      | 1.2     |
|                 | 0.35 | 1716| 2404  | 187    | 13   | 2310   | 72.3        | 24.8     | 0.8      | 2.1     |

Conditions: wood biomass, 150 mg/min (H$_2$O 9.6%, C, 5880 mol/min; H, 8140 mol/min; O, 3390 mol/min); O$_2$ 37 ml/min; N$_2$ 150 ml/min; catalyst 1 g, reaction temperature 873 K.
Furthermore, we characterized two catalysts by means of H₂ adsorption amount for the estimation of the dispersion. The results are listed in Table 5. Rh particles are more highly dispersed than Ni particles. On the other hand, the number of surface Ni atoms on Ni catalyst is twice as large as that of Rh atoms on Rh/CeO₂/SiO₂. In addition, TEM image of reduced Rh/CeO₂/SiO₂ is shown in Fig. 11. Black small particle can be assigned to Rh metal particles, and the average diameter is estimated to be 6 nm, which agrees with estimation from adsorption measurement. It is found that Rh metal particles are present on both SiO₂, which has very low contrast, and CeO₂/SiO₂, whose contrast is medium level. On Rh/CeO₂/SiO₂, large crystal of CeO₂ was not observed. From the X-ray diffraction analysis, the crystal size of CeO₂ is estimated to be 8 nm. Although it is known that CeO₂ is easily sintered [39]. It is possible to maintain small crystal size by the presence of inert SiO₂. In contrast, Ni catalyst has low dispersion because of larger loading amount of Ni and lower BET surface area. Although the number of surface atoms of Ni on Ni catalyst was twice of that on Rh catalyst, the performance of Rh/CeO₂/SiO₂ was clearly higher than that of Ni catalyst. As reported previously, Rh/SiO₂ and CeO₂/SiO₂ were not good catalysts [40,41], and these indicate that the synergy of Rh and CeO₂ is very important.

In our fluidized bed system for partial oxidation of tar, the catalyst particles can be circulated between oxidizing and reducing parts as illustrated in Fig. 10. Therefore, the catalyst can be oxidized and reduced under corresponding conditions. Usually, Ni and Rh can be easily oxidized, on the other hand, it is expected that catalyst reducibility is different [41]. The catalyst reducibility is evaluated by

| Catalyst          | Feeding rate (mg/min) | Formation rate (µmol/min) | CO | H₂ | CH₄ | C₂ | CO₂ | C-conv. (%) | Char (%) | Coke (%) | Tar (%) |
|-------------------|-----------------------|----------------------------|----|----|-----|----|-----|-------------|----------|----------|--------|
| Rh/CeO₂/SiO₂      | 150                   | 2424                       | 2835 | 249 | 0   | 1814 | 76.7 | 22.3 | 1.0 | 0.0 |
|                   | 200                   | 3099                       | 3740 | 407 | 0   | 2444 | 76.3 | 18.2 | 1.5 | 3.3 |
|                   | 250                   | 3924                       | 4920 | 444 | 0   | 2996 | 75.6 | 18.2 | 2.2 | 4.0 |
| Steam reforming   | 150                   | 1761                       | 2463 | 215 | 75  | 1991 | 70.4 | 24.9 | 3.5 | 1.2 |
| Ni catalyst       | 200                   | 2399                       | 3301 | 301 | 0   | 2340 | 64.7 | 24.9 | 4.1 | 6.3 |
|                   | 250                   | 2665                       | 3442 | 506 | 102 | 2491 | 60.2 | 22.3 | 8.0 | 9.5 |

Conditions: wood biomass, 150–250 mg/min (H₂O 9.6%, C, 5880–9880 mol/min; H, 8140–13600 mol/min; O, 3390–5650 mol/min); O₂ 37–62 ml/min; N₂ 150 ml/min; catalyst 1 g, ER = 0.25, reaction temperature 873 K.
means of TPR. Fig. 12 shows the TPR profiles of Rh/CeO2/SiO2, CeO2/SiO2 and Ni catalyst. The Ni catalyst started to be reduced at 700 K, and Rh/CeO2/SiO2 catalyst started at 400 K. This is related to be the reducibility of metal component [42]. The consumption of hydrogen was 1.0, 0.8, 2.0 mmol/g-cat on Rh/CeO2/SiO2, CeO2/SiO2 and Ni catalyst, respectively. Since 0.12 mmol/g-cat Rh is present on Rh/CeO2/SiO2 catalyst, 0.18 mmol/g-cat H2 can be used for the reduction of Rh on the basis of Rh2O3+3H2→2Rh+3H2O. The difference between 1.0 and 0.18 mmol/g-cat can be assigned to reduction of Ce species. From the comparison between Rh/CeO2/SiO2 and CeO2/SiO2, it is found that the presence of Rh enhanced the reduction of CeO2/SiO2. Rh/CeO2/SiO2 has the higher reducibility than Ni catalyst, and this can contribute to the enhancement of the amount ratio of reduced catalyst to oxidized catalyst in fluidized bed reactor. Furthermore, from the TPR results, it should be noted that Rh species can interact with CeO2 species intimately, and this can be related to high combustion activity. It has been reported that Rh2O3 and CeO2 can form solid solution, and this can give high combustion activity [43]. In order to elucidate the mechanism of high combustion activity, further investigation is necessary.

### 4. Conclusion

(1) Various materials such as Rh/CeO2/SiO2, steam reforming Ni catalyst, active clay, USY zeolite, MS-13×, dolomite, alumina, silica sand, fluorite and non-

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Table 5

| Catalyst          | Surface area (m²/g) | Metal loading (10⁻⁴ mol/g-cat) | H2 adsorption (10⁻⁶ mol/g-cat) | Dispersion (%)<sup>a</sup> | Particle size (nm) |
|-------------------|----------------------|--------------------------------|--------------------------------|-----------------------------|--------------------|
| Rh/CeO2/SiO2      | 323                  | 1.2                            | 10.4                           | 17.3                        | 6.3                |
| Ni catalyst       | 9.0                  | 20.4                           | 20.3                           | 2.0                         | 48.7               |

<sup>a</sup> Calculated by the ratio of 2 (H₂ adsorption) to metal loading on the basis of H/Ms = 1.
catalyst, were tested for the partial oxidation of tar from wood biomass (architectural salvage). Rh/CeO$_2$/SiO$_2$ and steam reforming Ni catalyst were much more effective than other materials in the partial oxidation of tar to CO and hydrogen.

(2) From the investigation on the dependence of reaction temperature, ER, and biomass feeding rate, Rh/CeO$_2$/SiO$_2$ exhibited higher performance in the partial oxidation of tar than the Ni catalyst, especially in terms of the decrease of tar and coke amount.

(3) Catalyst stability of Rh/CeO$_2$/SiO$_2$ was higher than that of the Ni catalyst. The deactivation can be due to the coke deposition. This indicates that Rh/CeO$_2$/SiO$_2$ has high resistance to coke formation during the reaction.

(4) In the fluidized bed reactor for the partial oxidation of tar, the catalyst particles can be circulated in oxidizing and reducing atmosphere. In reducing atmosphere, the catalyst is in reduced state and it can contribute to reforming of tar with steam. On the other hand, in oxidizing atmosphere, the catalyst is in oxidized state, and it can contribute to combustion of coke and tar with oxygen.

(5) From the activity test of methane combustion, Rh/CeO$_2$/SiO$_2$ had much higher activity than the Ni catalyst. This supports high resistance of Rh/CeO$_2$/SiO$_2$ to coke formation.

(6) From the TPR profiles, Rh/CeO$_2$/SiO$_2$ had higher reducibility than Ni catalyst. This is related to enhancement ratio of reduced catalyst amount to oxidized catalyst amount in the fluidized bed reactor.

(7) From the comparison between Rh/CeO$_2$/SiO$_2$ and CeO$_2$/SiO$_2$ in TPR profiles, a part of CeO$_2$/SiO$_2$ has intimate interaction with Rh species. The presence of Rh promoted the reduction of CeO$_2$ drastically, and this can be related to high combustion activity caused by the synergy between Rh and CeO$_2$.

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