Available online at www.sciencedirect.com

Catalysis Today 115 (2006) 254–262

www.elsevier.com/locate/cattod

Catalytic performance of supported Ni catalysts in partial oxidation and steam reforming of tar derived from the pyrolysis of wood biomass

Tomohisa Miyazawa, Takeo Kimura, Jin Nishikawa, Shigeru Kado, Kimio Kunimori, Keiichi Tomishige *

Institute of Material Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Abstract

Activity test of Ni/Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/CeO_2 and Ni/MgO catalysts in the partial oxidation (POT) and steam reforming of tar (SRT) derived from the pyrolysis of cedar wood was performed. In these activity tests, the order of the performance in both reactions was similar. Catalyst characterization was also carried out by means of H_2 adsorption, TPR and XRD. From the combination of catalyst characterization with the results of the activity tests, it is suggested that the conversion of tar in POT and SRT is mainly controlled by the number of surface Ni metal. In addition, Ni/CeO_2 showed smaller amount of coke than other catalysts in the POT and SRT. From the TGA profiles of active carbon mixed with catalysts, it is found that Ni/CeO_2 promoted the reaction of active carbon with O_2 and steam. The function of the fluidized bed reactor in the POT with respect to coke and tar amount was discussed.

Keywords: Partial oxidation; Steam reforming; Tar; Biomass; Ni; Combustion; Fluidized bed reactor

1. Introduction

Biomass can be an abundantly available and renewable energy resource. Hydrogen and synthesis gas production from biomass contributes to environmental protection by the decrease of CO_2 emissions. This is because the synthesis gas can be converted to clean liquid fuels, such as methanol, and Fischer-Tropsch oil. A lot of attention has also been paid to fuel cells and hydrogen society. In particular, hydrogen derived from biomass can be also regarded as renewable hydrogen. One of the conventional methods for the production of hydrogen and syngas from biomass is the non-catalytic gasification of biomass with air [1]. The demerit of this non-catalytic gasification is high reaction temperature above 1273 K, and this can decrease the total energy efficiency of this process [2]. However, the decrease of tar content in the product gas needs high reaction temperature [3].

In order to decrease the tar content, dolomite, olivine, and silica sand have been used as catalysts, however, the effect was not so significant and the reaction temperature was almost the same as that of non-catalytic gasification. The utilization of metal catalysts in the biomass gasification system is an effective approach to reduce the tar content in the product gas as well as to improve the product gas composition [4–6].

Recently, we have developed $Rh/CeO_2/SiO_2$ catalyst for the gasification of cellulose and biomass with air [7–21]. It is found that $Rh/CeO_2/SiO_2$ was much more effective catalyst for the gasification of biomass than conventional steam reforming Ni catalyst and dolomite [7–11]. In the case of gasification of cedar wood with air using $Rh/CeO_2/SiO_2$ and a fluidized bed reactor, the tar content decreased drastically and the amount of carbon deposition was very small even at 823 K [12–21]. On the other hand, $Rh/CeO_2/SiO_2$ has some problems in high cost and limited availability due to the utilization of Rh. One of the promising metal components is Ni. However, in most reports, commercial Ni catalysts, which were developed for steam reforming of methane and hydrocarbons, have been tested and the performance was not satisfactory. In some cases, catalysts

---

* Corresponding author. Tel.: +81 298 53 5030; fax: +81 298 53 5030.
E-mail address: tomi@tulip.sannet.ne.jp (K. Tomishige).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.055

for the gasification of biomass have been developed [22–25], however, the investigations are limited [2].

The fundamental investigation on the catalytic performance of various Ni catalysts can contribute to the catalysts development for the gasification of biomass, since the investigation is so limited at present. In particular, this research focuses on the catalytic performance of oxide supported Ni catalysts in the partial oxidation and steam reforming of tar derived from the pyrolysis of cedar wood.

2. Experimental

2.1. Catalyst

We prepared Ni catalysts using various oxides as catalyst support. The oxides used in this research were MgO (Ube materials), Al_2O_3 (JRC-ALO4), CeO_2 (Wako Pure Chemical Industries), ZrO_2 (Soekawa Chemicals) and TiO_2 (Aerosil P-25). Before loading of Ni, support materials were calcined under air atmosphere. Calcination temperatures and times are listed in Table 1. The loading of Ni was carried out by the incipient wetness method using the aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries). The support material is impregnated with the aqueous solution of Ni to fill the pores completely. Addition of the solution was stopped when the solid tends to become sticky. In this condition, the volume of the solution adsorbed by the support is thought to become equal to the pore volume. After this, the sample was dried at 383 K for 0.5 h. These procedures were repeated until the loading amount of Ni reached 12 wt.%. After loading the Ni salt on the support, the samples were dried at 383 K for 12 h, followed by the calcination at 773 K for 3 h under air atmosphere. The catalysts were pressed into disk, crushed and sieved to granules with the size of 0.08–0.35 mm.

2.2. Biomass

Cedar wood was ground with a ball mill to about 0.1–0.3 mm size. The moisture content of the cedar wood was 9.2%. The dry-based composition by weight was C 51.1%, H 5.9%, O 42.5%, N 0.1%, and ash 0.3%. The elemental analysis was carried out by the Japan Institute of Energy.

2.3. Activity test in partial oxidation and steam reforming of tar

Two types of catalytic activity tests were carried out in a laboratory-scale continuous feeding dual-bed reactor as shown in Fig. 1. One was the partial oxidation of tar (POT) with O_2, the other was the steam reforming of tar (SRT). The reactor contained the primary bed for pyrolysis of biomass and accumulation of solid products in the pyrolysis reaction such as char and ash. The gaseous products at reaction temperature including tar were introduced to the secondary catalyst bed. Tar is liquid at room temperature, and it is a mixture of various hydrocarbons and oxygenates. We have already analyzed tar from the pyrolysis of cedar wood in our previous report [21]. At reaction temperature, tar can be vaporized and 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.

The reactor had four ports for gas introduction and one port for the effluent gas. We introduced gases from each port for the evaluation of catalytic performance. In the evaluation of catalytic performance in the POT, oxygen was introduced into the catalyst bed through the thin tube in the inner reactor (port A), and N_2 was also fed from the bottom of the outer reactor through a quartz distributor. In this case, the reaction between tar and O_2 proceeds in the catalyst bed. In the evaluation of catalytic performance in the SRT, no gas was introduced from the port A, and N_2 was also fed from the bottom of the outer reactor through a quartz distributor. At the same time, steam was supplied to the reactor using a microsyringe through a thin tube in the reactor (port D). Feeding rates of gases, steam and biomass are described for each result. In the POT, the catalyst granules can move freely, and it corresponds to the fluidized bed under the reaction conditions. In the SRT, the catalyst fluidization is inhibited by putting quartz wool on the catalyst bed, and it corresponds to the fixed bed reactor. In the both reactions, carbon-containing solid byproducts were observed. Here, the solid carbon deposited on the catalysts is called coke. In order to estimate the yield of this coke, after the biomass feeding was stopped, oxygen (36 ml/min) was supplied from

Table 1
Characterization results of fresh Ni catalysts

Catalyst[a]	Calcination temperature and time (K, h)	BET surface area (m^2/g)	Adsorption amount of H_2 (10^{-6} mol g cat^{-1})	Reduction degree from TPR (%)	Dispersion[b] (%)	Particle size of Ni (nm)	
						H_2 adsorption[c]	XRD[d]
Ni/Al_2O_3	1423, 1	8	27	106	2.7	36	31
Ni/ZrO_2	1073, 3	10	30	96	3.0	31	29
Ni/TiO_2	1173, 3	16	28	97	2.8	34	21
Ni/CeO_2	1073, 3	12	17	106	1.7	56	58
Ni/MgO	–[e]	12	3	20	0.3	381	N.D.

[a] Loading amount of Ni: 2.0×10^{-3} mol g cat^{-1}.
[b] Dispersion calculated by 2 × (adsorption amount of H_2)/(loading amount of Ni)/(reduction degree) × 100.
[c] Particle size of Ni calculated by (97.1 nm)/(dispersion %) [33,34].
[d] Particle size of Ni calculated from Scherrer equation, using the half-width at half-height of the strong intensity metal peak [35,36].
[e] MgO support was used without precalcination.

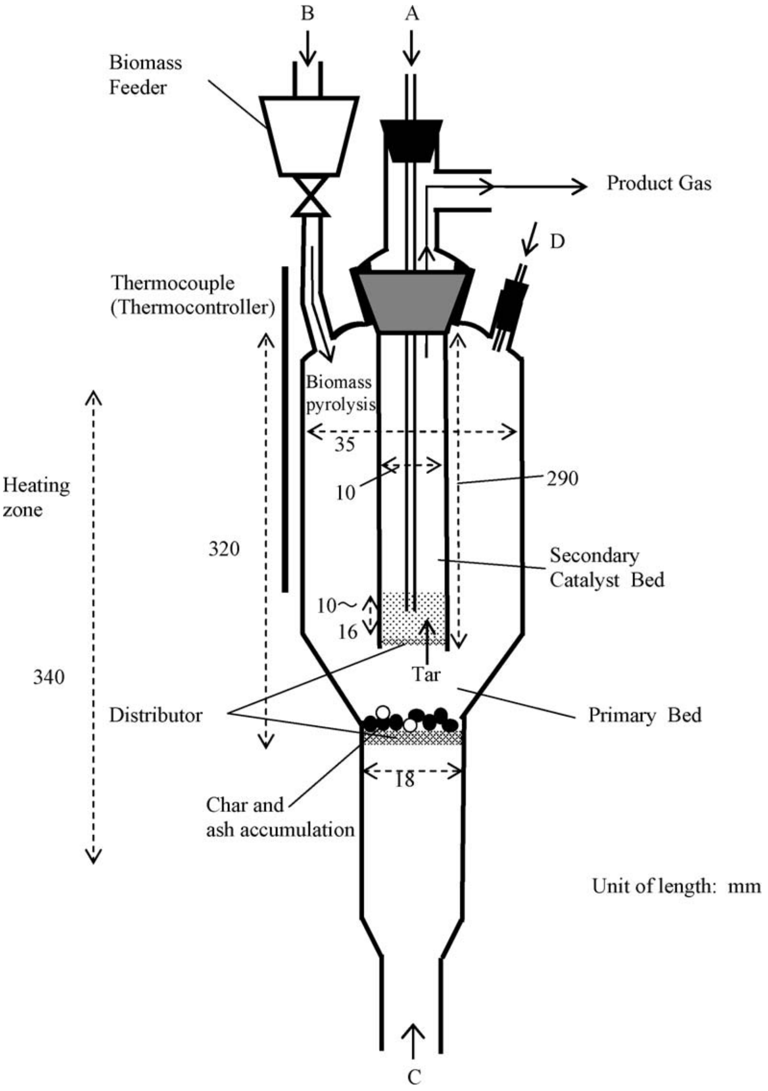

Fig. 1. Schematic diagram of the reactor. Activity test in POT from biomass A: O_2, B: N_2 + biomass, C: N_2, D: None; activity test in SRT from biomass A: None, B: N_2 + biomass, C: N_2, D: steam; coke estimation A: O_2, B: N_2, C: N_2, D: None; char estimation A: None, B: N_2, C: $O_2 + N_2$, D: None.

port A, and N_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_2 with a small amount of CO. Coke amount can be estimated from the total amount of $CO_2 + CO$. Furthermore, in the estimation of yield of char, which is formed from the pyrolysis of biomass before contacting with catalysts, the gas from port C was changed to $O_2 + N_2$ (36 + 100 ml/min), and N_2 (50 ml/min) was introduced from port B. In this treatment, the reaction of char with O_2 can proceed to form CO_2 with a small amount of CO. The yield of char was estimated from $CO_2 + CO$ on the basis of this procedure. The reactor temperature was controlled by a thermocouple positioned outside the reactor as shown in Fig. 1. The tests were carried out under atmospheric pressure by using 1 g of fresh catalyst. Before the test, the catalyst was pretreated under H_2 stream of 40 ml/min at 773 K for 0.5 h. H_2 was introduced from port C, and no gas was introduced from other ports in this pretreatment.

The effluent gas went through the filter and an iced water condenser in order to remove any solid and liquid materials contained in the product gas, and it was collected by a syringe and analyzed by gas chromatograph (GC). The concentrations of CO, CO_2, CH_4 and C_2 (ethane and ethylene) were determined by a FID-GC equipped with a methanator and that of H_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 "$A/B \times 100$", where A represents the formation rate of $CO + CO_2 + CH_4 + C_2$ 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 $CO_2 + CO$ in the combustion)/(total carbon amount in fed biomass). As a result, we can measure the yield of gaseous products and solid products (coke and char). On the other hand, 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. We estimated the tar yield by subtraction of gaseous and solid product yields from the total, that is the yield of tar is defined as (100 – C-conv. (%) – coke yield (%) – char yield (%)). Equivalence ratio (ER) can be calculated by the ratio of feeding oxygen to oxygen for complete combustion of biomass in the POT.

2.4. *Catalyst characterization*

Surface area of catalysts is measured by BET method. Chemisorption experiments were carried out in a high-vacuum system by volumetric methods. Before H_2 adsorption measurement, the catalysts were treated in H_2 at 773 K for 0.5 h. H_2 adsorption was performed at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The sample weight was about 0.2 g. The dead volume of the apparatus was about 60 cm^3. Dispersion was calculated based on the total H_2 adsorption.

Thermogravimetric analysis (TGA) of active carbon Black Pearls 2000 (Cabot, surface area: 1500 m^2/g) mixed with or without catalysts was carried out by using DTA-60 (Shimadzu). Weight of the sample is about 5 mg of active carbon + 5 mg of catalyst. TGA was measured under the flowing air (20 ml/min) or N_2 + steam (20 ml/min, 5% steam) and the heating rate was 15 K/min (300–1273 K).

Temperature-programmed reduction (TPR) with H_2 was performed in a fixed-bed flow reactor. The TPR profile of each sample was recorded from room temperature to 973 K under a flow of 5.0% H_2/Ar. The flow rate of 5.0% H_2/Ar was 30 ml/min, and the catalyst weight was 150 mg. The heating rate was 10 K/min and the temperature was maintained at 973 K for 30 min after it reached 973 K. The consumption of H_2 was monitored continuously with a TCD gas chromatograph equipped with a frozen acetone trap in order to remove H_2O from the effluent gas.

X-ray powder diffraction (XRD) spectra were recorded in a Philips X'pert diffractometer. Cu Kα (λ = 0.154 nm, 40 kV, 20 mA) radiation was used as X-ray source. Scanning was conducted over the range of $2\theta = 5–75^\circ$. XRD patterns of reduced catalysts were collected under air atmosphere.

3. Results and discussion

3.1. *Activity test in POT and SRT*

Catalytic performance of various Ni catalysts and no catalyst in POT derived from the pyrolysis of cedar wood at 823–923 K was investigated. In these activity tests, the formation of products was observed for 15 min, and significant deactivation was not observed for any of the catalysts. The data of formation rate of the gaseous products listed in Table 2 corresponds to the average during 15 min. In the case of no 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 the formation rate of CO and H_2 was small, and H_2/CO ratio was also small. The amount of char was almost constant in all the cases. This is because the char is accumulated in the primary bed without contact to the catalyst particles. On the other hand, when Ni catalysts were used, the formation rate of gaseous products, especially H_2, increased drastically compared to no catalyst. The yield of tar decreased. This result indicates that Ni catalysts are effective to the conversion of tar to useful gases such as CO and hydrogen, although the performance was strongly dependent on support materials.

Table 2
Catalyst performance in partial oxidation of tar derived from biomass

Catalyst	*T* (K)	Formation rate (μmol/min)					H_2/CO	C-conv. (%)	Char (%)	Coke (%)	Tar (%)
		CO	H_2	CH_4	C_2	CO_2					
Ni/Al_2O_3	823	1437	1813	270	3	2238	1.3	65	25	4.2	5.8
	873	2194	2497	225	0	2238	1.1	76	21	3.0	0.0
	923	2719	2844	114	0	2080	1.0	80	19	1.0	0.0
Ni/ZrO_2	823	1560	1313	550	246	1527	0.8	68	22	2.5	7.5
	873	1987	1553	682	43	1683	0.8	73	22	2.3	2.7
	923	2537	1914	802	33	1537	0.8	81	18	1.0	0.0
Ni/TiO_2	823	1516	1362	310	10	2098	0.9	65	23	3.0	9.0
	873	1922	1688	426	0	2019	0.9	71	24	2.9	2.1
	923	2191	2366	422	0	2054	1.1	76	23	1.0	0.0
Ni/CeO_2	823	1338	650	321	50	2100	0.5	63	24	1.3	11.7
	873	1905	1165	396	5	2027	0.6	71	23	0.9	5.1
	923	2379	1399	524	0	1964	0.6	79	20	1.0	0.0
Ni/MgO	823	1221	585	335	36	1648	0.5	54	23	2.9	20.1
	873	1658	914	356	91	1630	0.6	63	19	3.3	14.7
	923	2155	1459	582	31	1859	0.7	76	21	2.2	0.8
No catalyst	823	972	143	238	0	1772	0.1	46	25	0.0	29.0
	873	1251	263	307	40	1789	0.2	53	24	0.0	23.0
	923	1441	413	482	108	2394	0.3	70	21	0.0	9.0

Conditions: biomass; 150 mg/min (H_2O 9.2%; C 5800 μmol/min; H 8040 μmol/min; O 3580 μmol/min); gas introduction: (A) O_2 36 ml/min; (B) N_2 50 ml/min; (C) N_2 100 ml/min; catalyst 1 g, ER = 0.25.

Table 3
Catalyst performance in steam reforming of tar derived from biomass

Catalyst	*T* (K)	Formation rate (μmol/min)					H_2/CO	C-conv. (%)	Char (%)	Coke (%)	Tar (%)
		CO	H_2	CH_4	C_2	CO_2					
Ni/Al_2O_3	823	706	938	157	48	420	1.3	59	19	12.7	9.3
	873	786	2087	115	0	677	2.7	68	18	10.9	3.1
	923	1038	2484	42	6	561	2.4	71	18	11.0	0.0
Ni/ZrO_2	823	615	1222	95	17	559	2.0	59	22	6.6	12.4
	873	764	1498	96	0	479	2.0	62	22	6.1	9.9
	923	1024	1991	79	0	687	1.9	77	19	4.0	0.0
Ni/TiO_2	823	624	950	142	31	411	1.5	53	19	15.1	12.9
	873	733	1768	136	0	717	2.4	68	17	9.9	5.1
	923	1051	2455	78	0	697	2.3	77	16	7.0	0.0
Ni/CeO_2	823	565	781	121	40	349	1.4	50	20	4.3	25.7
	873	1008	1077	178	54	310	1.1	69	17	4.0	10.0
	923	967	1775	124	56	499	1.8	73	17	3.1	6.9
Ni/MgO	823	569	417	142	36	251	0.7	45	16	10.4	28.6
	873	750	585	150	59	197	0.8	52	17	10.0	21.0
	923	842	695	207	94	302	0.8	66	16	8.0	10.0
No catalyst	823	603	269	132	66	189	0.4	45	24	0.0	31.0
	873	649	265	210	88	192	0.4	53	21	0.0	26.0
	923	902	294	295	104	243	0.3	71	17	0.0	12.0

Conditions: biomass; 60 mg/min (H_2O 9.2%; C 2320 μmol/min; H 3220 μmol/min; O 1430 μmol/min); gas introduction: (A) none; (B) N_2 50 ml/min; (C) N_2 50 ml/min; (D) steam 1110 μmol/min; catalyst 1 g, $H_2O/C = 0.5$.

Catalytic performance of various Ni catalysts and no catalyst in the SRT derived from the pyrolysis of cedar wood at 823–923 K is listed in Table 3. Biomass feeding rate in the SRT is lower than that in the POT. This is because the reaction rate of SRT is lower than that of POT. Therefore the biomass feeding rate was adjusted for the comparison of the catalyst performance. Without catalyst, the large amount of tar was also observed in the SRT. The formation rate of gaseous products on no catalyst in the SRT was much smaller than those in the POT, and this can be due to the difference of the feeding rate of cedar wood. In contrast, char yield in the SRT was little lower than in the POT. This can be because steam prohibits char formation. In terms of conversion in the SRT, the order of the performance at 823 K was as follows: $Ni/Al_2O_3 > Ni/ZrO_2 > Ni/TiO_2 > Ni/CeO_2 > Ni/MgO >$ no catalyst. This trend in the SRT is the same as in the POT. This suggests that the performance in the POT can be reflected by the steam reforming activity. Tar amount on the basis of carbon in the SRT was much larger than that in the POT. This indicates that partial oxidation is more effective in tar conversion than steam reforming reaction.

In addition, the coke yield in the SRT was much higher than that in the POT. This can be explained by the role of fluidized bed reactor combined with O_2. According to our previous reports [26,27], catalytic fluidization in oxidative reforming of methane under pressurized conditions, where coke can be easily formed, can decrease coke amount drastically. This suggests that coke can be removed by the reaction between coke and oxygen. The difference between the SRT and the POT in coke yield agrees with this explanation. It is characteristic that Ni/CeO_2 has high resistance to coke deposition at all the temperature. Furthermore, H_2/CO ratio in the SRT was higher than that in the POT because the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is promoted by the presence of steam.

The catalysts have been used under quite high temperature conditions, yet no severe deactivations were observed. Surface area of catalysts and metal particle size were maintained during the reactions. Although the deactivation can be observed in the longer life test, at present, only the initial activity for 15 min is evaluated.

3.2. Comparison of catalyst performance on the basis of characterization results

Fig. 2 shows the TPR profiles of various Ni catalysts. It is possible to estimate the reduction degree from the results of H_2 consumption in TPR profiles. The reduction degree is listed in Table 1. Except for Ni/MgO, the reduction degree of Ni was almost 1.0 and this indicates that all the Ni was reduced at about 800 K. On the other hand, the reduction degree of Ni/MgO was about only 0.2. This can be because the strong interaction between NiO and MgO decreases catalyst reducibility [28,29]. In order to estimate the number of surface Ni atom on Ni metal particles, the measurement of H_2 adsorption was carried out. The result is also listed in Table 1. The order of adsorption amount of H_2 was as follows: $Ni/ZrO_2 \geq Ni/TiO_2 \approx Ni/Al_2O_3 > Ni/CeO_2 > Ni/MgO$. Assuming that the stoichiometry of hydrogen atom to surface Ni atom is equal to 1, the dispersion of Ni metal particles can be calculated by the combination with the amount of reduced Ni, which is related to reduction degree from TPR results. Metal dispersion is also listed in Table 1. The dispersion over various Ni catalysts was rather low since the surface area was also low and the loading

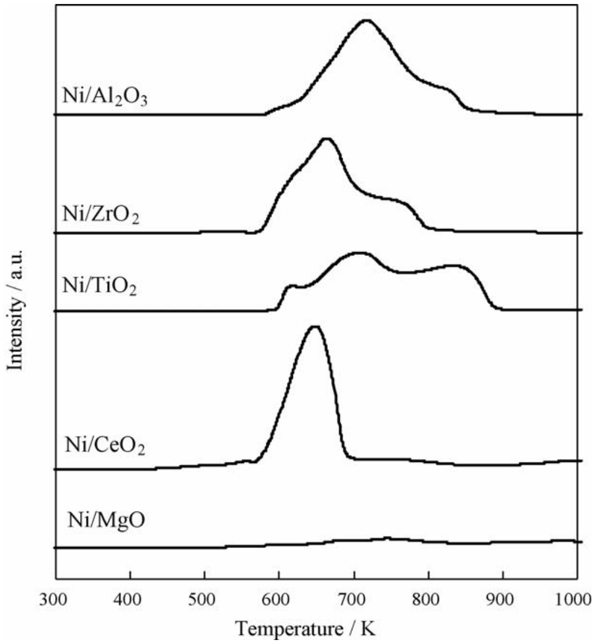

Fig. 2. TPR profiles of various Ni catalysts. Reaction condition: heating rate 10 K/min. Room temperature to 973 K, and the temperature was maintained at 973 K for 30 min. 5% H_2/Ar flow rate 30 ml/min.

amount of Ni was high. On the basis of the estimation of the dispersion, metal particle size can be determined. Metal particle size can also be determined from the peak at $2\theta = 44.3^\circ$, which is assigned to the diffraction of Ni(1 1 1) [30] in XRD patterns, using Scherrer equation. In the case of Ni/Al_2O_3, Ni/ZrO_2, and Ni/CeO_2, the particles sizes estimated by two methods agreed. In contrast, in the case of Ni/TiO_2, the particles size determined from XRD was smaller than that from H_2 adsorption. This can be explained by strong metal support interaction [31,32], where Ni particles are covered with partially reduced TiO_X. On the other hand, in the case of Ni/MgO, the peak assigned to Ni was not observed at all probably because the amount of reduced Ni is much smaller than other catalysts. On the basis of the characterization results, the relation between catalyst performance and properties can be discussed. Fig. 3a shows the relation between tar in POT at 823 K and the number of surface Ni atoms from H_2 adsorption on the assumption of $H/Ni_s = 1$. From the comparison, almost linear relation is observed, and this means that the catalyst with higher Ni dispersion is more effective to the conversion of tar in the POT.

Furthermore, Fig. 4a shows the relation between tar in SRT at 823 K and number of surface Ni atoms. In the case of SRT, almost linear relation is also observed. From these two comparisons, it is found that the performance of tar conversion is controlled by the number of Ni surface atoms in both POT and SRT reactions, and this means that support materials can play an important role on the enhancement of the metal dispersion.

Next the relation between coke and catalytic properties is discussed. Fig. 3b shows the relation between coke yield and number of surface Ni atoms on various catalysts in the POT. The tendency of coke yield is different from that of tar yield. Coke yield is not influenced by the number of surface Ni atoms.

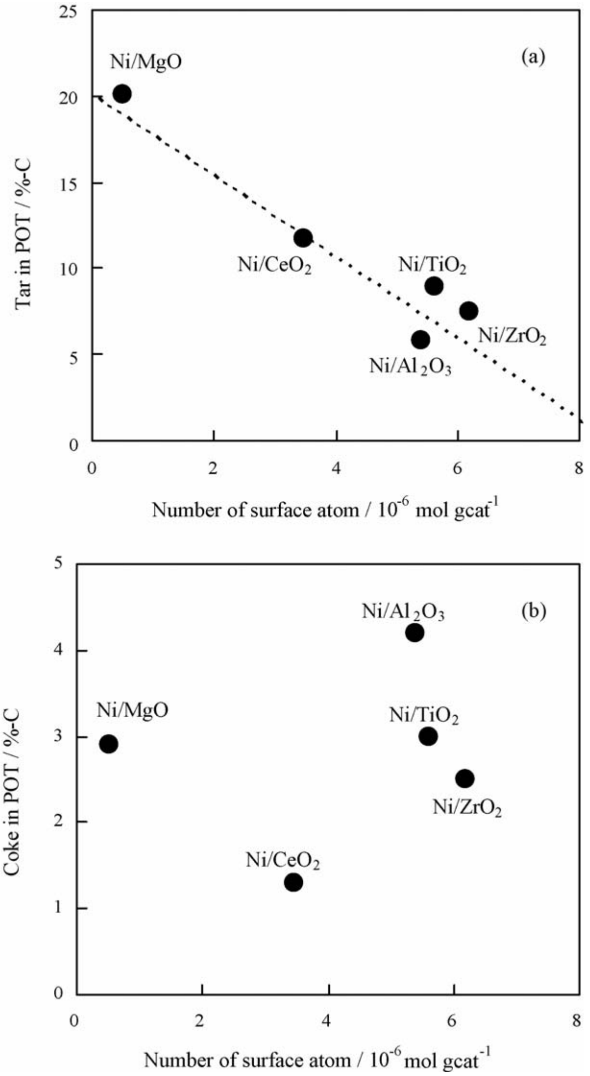

Fig. 3. Relation between (a) tar and (b) coke in the POT and the number of surface Ni atoms on various catalysts. Reaction conditions: wood biomass 150 mg/min (H_2O 9.2%, C 5800 μmol/min; H 8040 μmol/min; O 3580 μmol/min); O_2 36 ml/min; N_2 150 ml/min; catalyst 1 g, ER = 0.25, T = 823 K.

Fig. 4b shows the relation between coke yield and number of surface Ni atoms in the SRT. From the comparison between Figs. 3b and 4b, it is found that the tendency of coke yield is similar in both cases. In addition, it is characteristic that coke yield on Ni/CeO_2 was smaller than that on other Ni catalysts. These results indicate that coke yield can be strongly influenced by the properties of support materials, not by the number of surface Ni metal atom. These suggest that the coke yield can be dependent on the catalyst ability for coke removal. Therefore, we measured the reactivity of coke with catalysts using active carbon as a model compound of coke by means of thermogravimetric analysis. For the evaluation in POT, TGA profiles were obtained under flowing air, while for the evaluation in SRT, they were obtained under the presence of 5% steam. Fig. 5 shows TGA profiles of active carbon + catalyst under flowing air. In all the TGA curves weight loss can be assigned to exothermic profiles, and this can be due to combustion of active carbon. In the case of no catalyst,

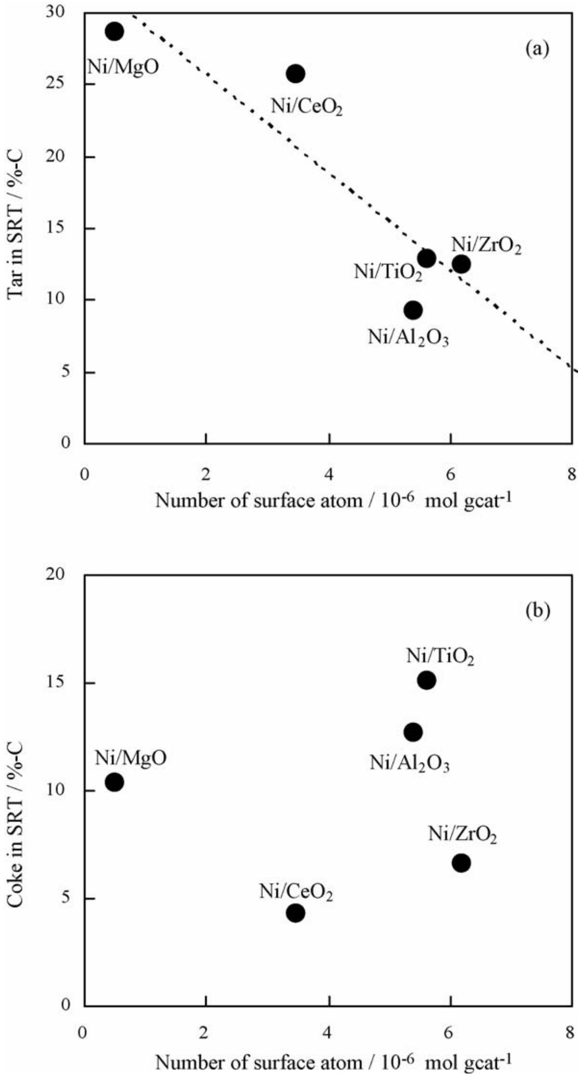

Fig. 4. Relation between (a) tar and (b) coke in the SRT and the number of surface Ni atoms. Reaction conditions: wood biomass 60 mg/min (H_2O 9.2%, C 2320 μmol/min; H 3220 μmol/min; O 1430 μmol/min). Gas introduction: A: none; B: N_2 50 ml/min; C: N_2 50 ml/min; D: N_2 50 ml/min + steam 1110 μmol/min; catalyst 1 g, $H_2O/C = 0.5$.

combustion reaction started above 900 K. In contrast, the addition of catalyst to active carbon clearly promoted combustion reaction. Especially Ni/CeO_2 showed higher performance than other Ni catalysts. In addition, the profile of CeO_2 is also shown in Fig. 5. It is found that CeO_2 itself has high combustion activity, and loading of Ni can also promote the combustion of active carbon. Except for Ni/CeO_2 catalyst, the performances of other Ni catalysts are similar. This high combustion activity on Ni/CeO_2 can be related to low coke yield in POT over Ni/CeO_2. In the POT using the fluidized bed reactor, catalyst granules have a chance to interact with oxygen near the O_2 introduction port. On the catalysts with high combustion performance, deposited coke can be removed by the combustion more easily.

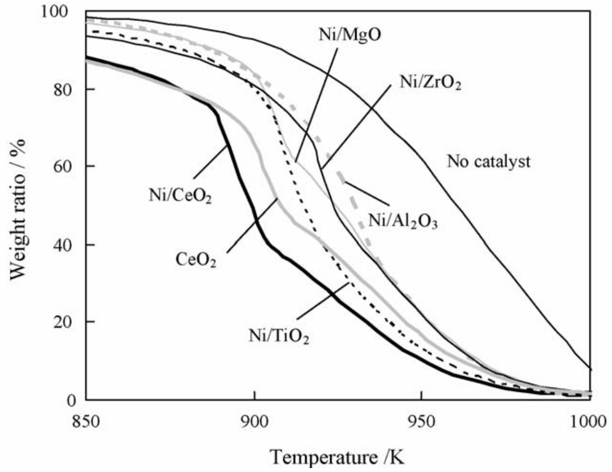

Fig. 5. Thermogravimetric analysis of active carbon mixed with catalysts under air atmosphere. Sample: 5 mg active carbon + 5 mg catalyst, heating rate = 15 K/min, room temperature to 1273 K, air flow rate, 20 ml/min.

Fig. 6 shows the TGA profiles of active carbon + catalyst in the presence of steam. In all these TGA profiles, weight loss gave endothermic profiles, which can be due to steam gasification of carbon. Compared to no catalyst, the presence of catalysts promoted steam gasification. The effect of Ni/CeO_2 was more significant than that of other catalysts. Ni/CeO_2 also exhibited low coke yield in the SRT, and this can be related to the promotion of reaction between steam and active carbon. In both cases, CeO_2 is very effective support for the inhibition of coke deposition. Especially, CeO_2 has high redox properties and oxygen storage capacity on the basis of $2CeO_2 \rightarrow Ce_2O_3 + 1/2O_2$ [37]. This is related to high performance in the removal of particulate matter from diesel engines. The role of CeO_2 support in POT can be explained by this function. On the other hand, even under the presence of steam, similar function of CeO_2 was observed. This suggests that reduced Ce species can be oxidized with steam, and CeO_2 can be regenerated. This regeneration of Ce^{4+} with steam requires much higher temperature than that with O_2 from the comparison between Figs. 5 and 6. The reactivity of carbon with O_2 is much higher than that with steam. This can reflect the amount of coke in the POT and SRT. In this research, the fluidized bed reactor was used in the POT. Model scheme of this

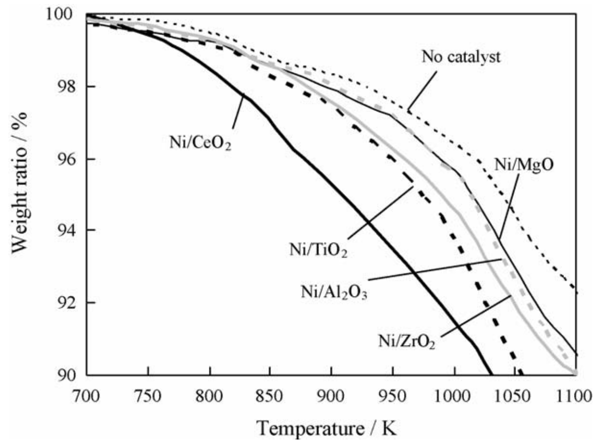

Fig. 6. Thermogravimetric analysis of active carbon mixed with catalysts under 5% steam/N_2 atmosphere. Sample: 5 mg active carbon + 5 mg catalyst, heating rate = 15 K/min, room temperature to 1273 K, gas flow rate 20 ml/min.

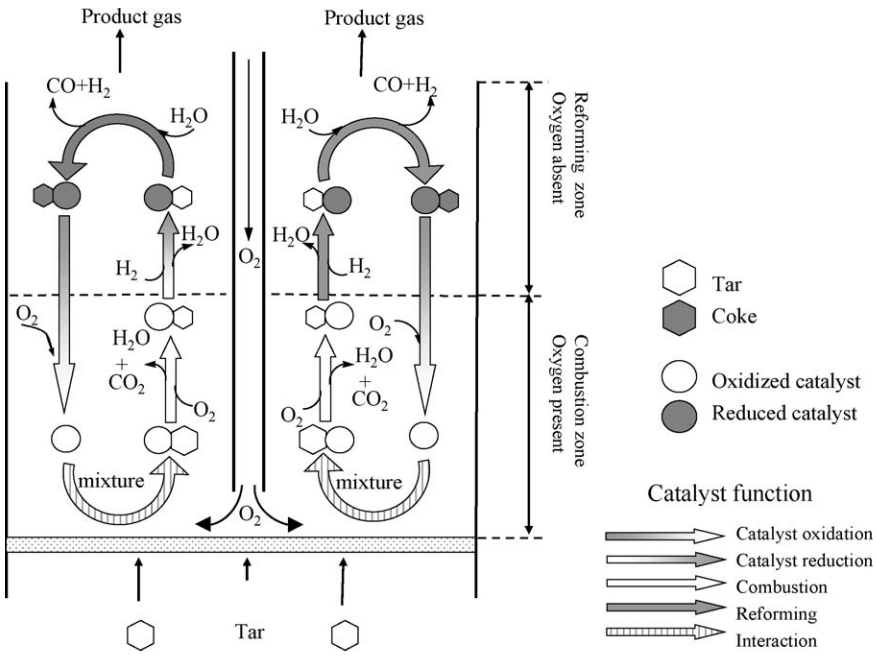

Fig. 7. A model scheme of partial oxidation of tar from the biomass in the fluidized bed reactor.

catalyst bed is illustrated in Fig. 7. Tar from the pyrolysis of cedar wood is supplied from the bottom of the reactor through the distributor, and oxygen is introduced near the bottom of the catalyst bed through thin tube. The amount of O_2 introduced is far from that for complete combustion of cedar wood and the tar. Therefore, O_2 is present near the bottom of the catalyst bed, however, in the upper part, O_2 is absent after the consumption. In the presence of oxygen, Ni metal is easily oxidized to NiO [38], and this catalyzes the combustion reaction. On the other hand, in the absence of oxygen, Ni metal catalyzes tar reforming. From the results in POT and SRT, the difference is coke yield. In the fluidized bed reactor for the POT, it is suggested that coke deposition can proceed in the reforming zone and the upper part of the reactor. In the SRT using fixed bed reactor, this coke can be removed only by the reaction with steam. In contrast, in the fluidized bed reactor, catalysts with deposited carbon have a chance to react with oxygen during the catalyst fluidization [26,27]. This can explain the smaller amount of coke in POT than that in SRT. The removal of coke during reaction is very important in terms of self cleaning of catalyst surface because carbon deposition can cause catalyst deactivation. In addition, tar amount in the POT was much smaller than that in SRT. This can be due to the high performance in coke removal in the POT.

4. Conclusion

(1) Ni/Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/CeO_2 and Ni/MgO catalysts were tested in the partial oxidation and steam reforming of tar derived from the pyrolysis of cedar wood. The order of the performance in both reactions is similar.
(2) From the combination of catalyst characterization by means of H_2 adsorption, TPR and XRD and the results of the activity tests, the conversion of tar in POT and SRT is mainly controlled by Ni metal, and the role of the support materials is for the dispersion of Ni metal.
(3) Regarding coke amount, Ni/CeO_2 showed smaller amount of coke than other catalysts in the POT and SRT. From the TGA profiles of active carbon mixed with catalysts, it is found that, Ni/CeO_2 promoted the reaction of active carbon with O_2 and steam, and this is one of the reasons of small coke yield of Ni/CeO_2.
(4) In the POT using the fluidized bed reactor, much higher tar conversion and lower coke yield were obtained than that in SRT using fixed bed reactor. Lower coke yield in POT can be explained by coke combustion with O_2 during the catalyst fluidization. This property is related to the self-cleaning of the catalyst surface, furthermore, this effect can enhance the tar conversion via the inhibition of catalyst deactivation.

Acknowledgements

This research has been supported by 21st Century COE Program and Grant in Aid for Young Scientists (A) under the Ministry of Education, Culture, Sports, Science and partially supported by Grant-in-Aid for JSPS Fellows.

References

[1] A.V. Bridgwater, Appl. Catal. A Gen. 116 (1994) 5.
[2] L. Devi, K.J. Ptasinski, F.J.J.G. Janssen, Biomass Bioenergy 24 (2003) 125.
[3] D. Sutton, B. Kelleher, J.R.H. Ross, Fuel Proc. Technol. 73 (2001) 155.
[4] J. Corella, J.M. Toledo, R. Padilla, Ind. Eng. Chem. Res. 43 (2004) 2433.
[5] R. Zhang, R.C. Brown, A. Suby, K. Cummer, Energ. Conserv. Manage. 45 (2004) 995.
[6] M.P. Aznar, M.A. Caballero, J. Gil, J.A. Martin, J. Corella, Ind. Eng. Chem. Res. 37 (1998) 37.

[7] M. Asadullah, K. Tomishige, K. Fujimoto, Catal. Commun. 2 (2001) 63.
[8] M. Asadullah, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, J. Catal. 208 (2002) 255.
[9] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, Green Chem. 4 (2002) 385.
[10] M. Asadullah, S. Ito, K. Kunimori, K. Tomishige, Ind. Eng. Chem. Res. 41 (2002) 4567.
[11] M. Asadullah, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, Environ. Sci. Technol. 36 (2002) 4476.
[12] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, K. Tomishige, Appl. Catal. A Gen. 246 (2003) 103.
[13] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, K. Tomishige, Energy Fuels 17 (2003) 842.
[14] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, K. Tomishige, Green Chem. 5 (2003) 399.
[15] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, Appl. Catal. A Gen. 255 (2003) 169.
[16] K. Tomishige, M. Asadullah, K. Kunimori, Catal. Surv. Asia 7 (2003) 219.
[17] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, S. Koyama, K. Tomishige, Biomass Bioenergy 26 (2004) 269.
[18] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, M. Yamada, K. Tomishige, Appl. Catal. A Gen. 267 (2004) 95.
[19] K. Tomishige, M. Asadullah, K. Kunimori, Catal. Today 89 (2004) 389.
[20] K. Tomishige, T. Miyazawa, T. Kimura, K. Kunimori, Catal. Commun. 6 (2005) 37.
[21] K. Tomishige, T. Miyazawa, T. Kimura, K. Kunimori, N. Koizumi, M. Yamada, Appl. Catal. B Environ. 60 (2005) 307.
[22] L. Garcia, A. Benedicto, E. Romeo, M.L. Salvador, J. Arauzo, R. Bilbao, Energy Fuels 16 (2002) 1222.
[23] J. Strinakruang, K. Sato, T. Vitidsant, K. Fujimoto, Catal. Commun. 6 (2005) 437.
[24] J. Corella, J.M. Toledo, R. Padilla, Ind. Eng. Chem. Res. 44 (2005) 2036.
[25] C. Courson, L. Udron, D. Świerczñski, C. Petit, A. Kiennemann, Catal. Today 76 (2002) 75.
[26] Y. Matsuo, Y. Yoshinaga, Y. Sekine, K. Tomishige, K. Fujimoto, Catal. Today 63 (2000) 439.
[27] K. Tomishige, Y. Matsuo, Y. Yoshinaga, Y. Sekine, M. Asadullah, K. Fujimoto, Appl. Catal. A Gen. 223 (2002) 225.
[28] K. Tomishige, Y.G. Chen, K. Fujimoto, J. Catal. 181 (1999) 91.
[29] Y.G. Chen, K. Tomishige, K. Yokoyama, K. Fujimoto, J. Catal. 184 (1999) 479.
[30] JCPDS Powder Diffraction File, International Centre for Diffraction Data, 2003.
[31] Y. Hiramoto, K. Kunimori, T. Uchijima, Nippon Kagaku Kaishi 2 (1993) 151.
[32] A. Dandekar, M.A. Vannice, J. Catal. 183 (1999) 344.
[33] C.H. Bartholomew, R.B. Pannell, J.L. Butler, J. Catal. 65 (1980) 335.
[34] F. Arena, B.A. Horrell, D.L. Cocke, A. Parmaliana, N. Giordano, J. Catal. 132 (1991) 58.
[35] Z. Hu, T. Wakasugi, A. Maeda, K. Kunimori, T. Uchijima, J. Catal. 127 (1991) 276.
[36] W.L. Bragg, The Crystalline State, G. Bell, London, 1933.
[37] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439.
[38] T.B. Reed, Free Energy Formation of Binary Compounds, MIT Press, Cambridge, 1971.