Production of Syngas by Catalytic Gasification of Biomass at Low Temperature and Synthesis of Clean Transportation Fuels

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Introduction

To save ourselves and our new generation from air pollution, the future energy resources should be clean and offer large potential benefits to reduce emissions of pollutants and greenhouse gases.[1-4] In this sense, hydrogen is one of the most promising candidates for future energy demand. However, the traditional method of hydrogen production is the high temperature steam reforming or the partial oxidation of the fossil resources such as methane, light hydrocarbons, naphtha and heavy oils.[5-9] To meet the growing demand of hydrogen and to prevent any energy-related problems, the alternative hydrogen sources, which should be renewable and sustainable, efficient and cost-effective, convenient and safe, must be developed and the production method also must be energy efficient.[10,11] Biomass can be considered as such a feed-stock. However, the hydrogen production from biomass gasification is problematic because of the formation of tar (complex mixture of higher hydrocarbons) and char during the gasification even at high temperature. In order to get the higher energy efficiency, when the process is carried out at lower temperature (<1123 K) more tar and char are produced. Use of catalyst can reduce the tar amount in the product gas even at low temperature. However, the conventional Ni based catalyst hardly reduces the tar and conversely the catalyst is suddenly deactivated due to deposition of carbon on the catalyst surface.[12] Thus, a novel catalyst with high performance and a suitable reactor are necessary for a highly efficient low-temperature process. We have developed and described here such a process for the cellulose gasification using the $Rh/CeO_2/SiO_2$ catalyst in a continuous-feeding fluidized-bed reactor at as low as 773 K.

Experimental

The gasification of cellulose was performed in a continuous-feeding fluidized-bed reactor. The reactor system is almost the same as batch feeding system, which is previously published.[13] However, the reactor dimension and feeding system have been modified for continuous-feeding gasification system. Here the gasification reactor is a quartz tube with the dimension of 66 cm high and 1.8 cm i.d. with a fluidized-bed section at the middle of the reactor. The cellulose feeder consisted of a glass vessel with a small pore at the bottom of about 0.5 mm diameter, allowing continuous feeding by vibrating the vessel with a vibrator. The vibration rate controlled the feeding rate. Cellulose particles (Merck, particle size 100~160 μm) were transported to the catalyst bed by the flow of N_2 gas through an inner tube of 5 mm i.d. Air and steam were introduced from the bottom of the reactor. Steam was supplied by using a microfeeder. The sample of the product gas was collected from the sampling port by micro-syringe and analyzed by Gas chromatograph (GC). The concentration of CO, CO_2, and CH_4 was determined by FID-GC and the concentration of hydrogen was determined by TCD-GC. The amount of char was determined by the amount of gas (mainly CO_2) formed after stopping the feed of cellulose under the air flowing at the reaction temperature.

CeO_2/SiO_2 was prepared by the incipient wetness method using the aqueous solution of $Ce(NH_4)_2(NO_3)_6$ and SiO_2 (Aerosil, 380 m^2/g). After drying at 393 K for 12 h, the catalyst was calcined at 773 K for 3 h under an air atmosphere. The Rh was loaded on CeO_2/SiO_2 by impregnation of the support with acetone solution of $Rh(C_5H_7O_2)_3$. The final catalyst was pressed, crushed and sieved to 150-250 μm particle size. Loading amount of CeO_2 is denoted in parenthesis using the weight percent. In each run, 3 g of catalyst was used and pretreated by a hydrogen flow at 773 K for 0.5 h. Composition of the commercial steam reforming catalyst (TOYO CCI, G-91) was 14 wt% Ni, 65-70 wt% Al_2O_3, 10-14 wt% CaO and 1.4-1.8 wt% K_2O. The composition of the dolomite was 21.0 wt% MgO, 30.0 wt% CaO, 0.7 wt% SiO_2, 0.1 wt% Fe_2O_3, and 0.5 wt% Al_2O_3. Before reaction the dolomite was calcined at 773 K for 3 h followed by a hydrogen treatment at 773 K for 0.5 h.

Results and Discussion

Initially, the gasification of cellulose was carried out on $Rh/CeO_2/SiO_2$ (35) and commercial steam reforming catalyst (G-91) at 773 K. The results are shown in Figure 1. The carbon conversion {C-conv = (formation rate of CO + CO_2 + CH_4) / (C-feeding rate in cellulose) x 100} to gas and formation of H_2, CO, CH_4, and CO_2 were stable on $Rh/CeO_2/SiO_2$ (35) (Figure 1a), however, on G-91 (Figure 1b) the C-conv decreased remarkably with time on stream. The rest of the carbon corresponds to the tar and char, which were deposited on the catalyst surface. When the cellulose feeding stopped after 25 min, the deposited carbon slowly converted to mainly CO_2 and this was much higher in the case of G-91 catalyst than that of $Rh/CeO_2/SiO_2$ (35). Here the total amount of CO_2 is assigned to the amount of char as listed in Table 1. On the lower active catalyst the char easily deposits and slowly takes part in the combustion reaction. So that the char can be build up on the lower active catalyst in the continuous feeding system and deactivates the catalyst as observed on G-91. In order to obtain a highly efficient catalyst, various kinds of Rh/CeO_2/M-type (M = SiO_2, Al_2O_3, and ZrO_2) catalysts with various loading of CeO_2 were prepared and tested in the gasification of cellulose in a continuous-feeding fluidized-bed reactor. As Table 1 shows, among the catalysts $Rh/CeO_2/SiO_2$ (35) exhibited the best performance with respect to the formation of syngas and/or hydrogen. As in the batch-feeding reaction,[13] the Rh/CeO_2 catalyst exhibited considerably high C-conv; however, the BET surface area drastically decreased after the reaction because of CeO_2 aggregation.[14] In the batch feeding gasification of cellulose, Pt, Ru, Pd, and Ni on CeO_2 and Rh on SiO_2, Al_2O_3, TiO_2, MgO, and ZrO_2 were also tested and the performance was lower than that of Rh/CeO_2. In the continuous feeding system, the Rh/CeO_2 catalyst suddenly deactivated due to decrease of surface area from 60 to 13 $m^2\ g^{-1}$. The loading of CeO_2 on the high surface SiO_2 inhibited the aggregation of CeO_2 and maintained the catalytic activity of $Rh/CeO_2/SiO_2$ (35). The loading amount of CeO_2 plays a major role for C-conv and we found that the 35 mass% of CeO_2 on SiO_2 is the best. In addition, no decrease of the BET surface area of this catalyst was observed. As Table 1, at a particular temperature such as 823 K, $Rh/CeO_2/SiO_2$ (35) shows much higher C-conv and syngas formation. Furthermore, the tar and char are much lower than that of other systems. These results clearly represent the novelty of $Rh/CeO_2/SiO_2$ (35) catalyst for cellulose gasification.

The results of the effect of temperature on the gasification of cellulose on $Rh/CeO_2/SiO_2$ (35), G-91, and dolomite catalysts and on the non-catalytic gasification and pyrolysis are listed in Table 1. The C-conv as well as the CO and H_2 formation is the

Table 1. Performance of Various Catalysts in the Gasification of Cellulose[a]

Catalyst	T /K	Formation rate /μmol min^{-1}				H_2/CO	C-conv	Char	Tar
		CO	H_2	CH_4	CO_2		/%[b]	/%[c]	/%[d]
$Rh/CeO_2/SiO_2$ (35)	773	845	1077	676	1178	1.3	86	6	8
	823	1250	1286	653	1050	1.1	94	4	2
	873	1617	1666	470	966	1.1	97	3	0
	923	1910	1995	335	865	1.1	99	1	0
	973	2279	2357	211	615	1.1	99	1	0
G-91	823	798	1538	418	1261	1.9	79	18	3
	873	1289	1858	393	1114	1.5	87	10	3
	973	2053	2242	158	762	1.1	94	3	3
Dolomite	823	414	112	72	747	0.3	39	34	25
	973	1149	892	294	336	0.8	57	14	29
	1073	1383	1072	410	833	0.8	83	4	13
	1173	1656	1442	515	750	0.9	93	2	5
None	823	240	76	15	562	0.3	26	7	67
	1023	1536	456	357	457	0.3	65	4	31
	1073	1714	505	462	417	0.3	82	3	15
	1173	1943	592	499	455	0.3	92	2	6
None[e]	823	228	62	11	39	0.3	9	15	76

[a]Conditions: Cellulose, 85 mg min^{-1} (C, 3148 μmol min^{-1}; H, 5245 μmol min^{-1}; O, 2623 μmol min^{-1}); Air, 50 cm^3 min^{-1}; N_2, 50 cm^3 min^{-1}; catalyst weight, 3 g; particle size of catalyst, 150-250 μm. [b]C conversion to gas = {(formation rate of CO + CO_2 + CH_4) / C-feeding rate} x 100. [c]Char% = (CO + CO_2 formation amount after stopping cellulose feeding / total C feeding) x 100. [d]Tar% = 100 - (C conversion% + char%). [e]Cellulose pyrolysis (N_2 flow, 50 cm^3 min^{-1} through distributor and 50 cm^3 min^{-1} with cellulose).

function of temperature and the catalyst activity. The increase of temperature favors the C-conv and syngas formation either in the catalytic or in the non-catalytic process. Thus, these are increased in all the systems with high temperature. On the other hand, the performance of the active catalyst also becomes higher with increasing temperature. Consequently the C-conv and syngas formation were improved drastically on $Rh/CeO_2/SiO_2$ (35) catalyst. About 94% carbon in the cellulose was converted to gas with a considerably high yield of CO and H_2 at as low as 823 K on $Rh/CeO_2/SiO_2$ (35) catalyst; however, this value was attained on G-91 catalyst at 973 K. Almost the complete C-conv was achieved at 923 K on $Rh/CeO_2/SiO_2$ (35). Methane was remarkably formed on the highly active $Rh/CeO_2/SiO_2$ (35) catalyst from the CO hydrogenation. On the other hand, the less C-conv was achieved on the dolomite and in non-catalyst system even at 1173 K. Especially, in the non-catalytic system, a very small amount of H_2 was formed. The reaction conditions of Table 1 were adjusted to the low temperature syngas production. In the hydrogen production system, the steam was introduced in order to proceed the steam reforming of tar and char and the water-gas shift reactions (H_2O + CO → CO_2 + H_2). The presence of steam in the reaction system facilitates the tar and char conversion to gas. Thus, in the next experiments, we added the various amounts of steam.

The C-conv as well as the selectivity of H_2 was dramatically improved by the steam addition (Figure 2) in the gasification of cellulose on $Rh/CeO_2/SiO_2$ (35) catalyst. In the absence of steam, 86% C-conv with a less hydrogen was achieved at 773 K, whereas interestingly enough, the 100% C-conv with the higher hydrogen formation was found when the steam with H_2O/C = 0.35 was introduced. Furthermore, the formation of hydrogen and CO_2 expectedly increased with increasing the H_2O/C ratio. The limit of the temperature was 773 K for the complete conversion of cellulose to gas products. No successful report was found for the cellulosic biomass gasification at such a low temperature. This result indicates that the steam directly takes part in the gasification of the tar and char on the highly active catalyst even at low temperatures, and thus complete C-conv was achieved at 773 K. The biomass derived tar can be converted to gas on the Ni-based catalysts in the secondary-bed reactor at above 1073 K;[15] however, in the primary-bed reactor the Ni-based catalysts suddenly deactivated by the carbon deposition,[16,17] and the similar phenomenon was observed for G-91.

Finally, the combination of the high performance of the $Rh/CeO_2/SiO_2$ (35) with the fluidized-bed reactor will provide the novel system for the hydrogen and syngas production from biomass at low temperature with a high-energy efficiency.

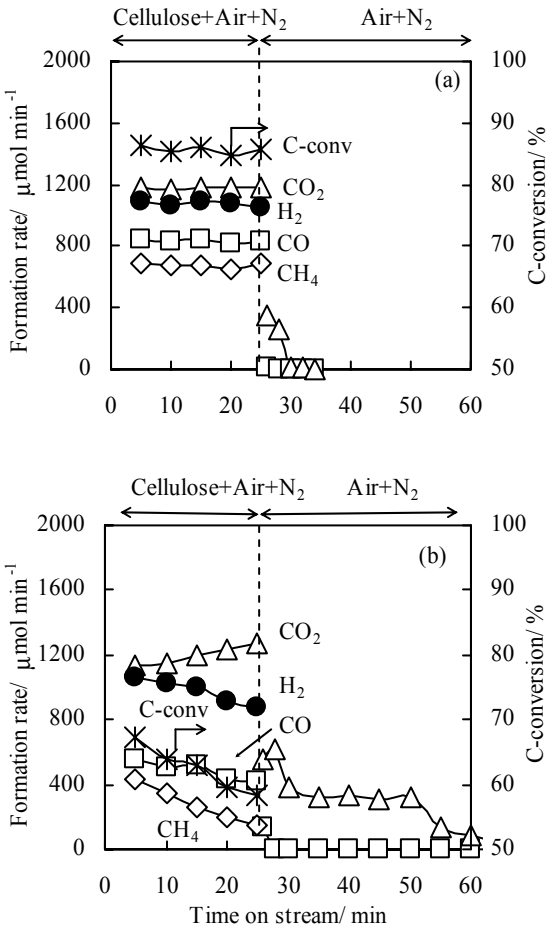

Figure 1. Dependence of time on stream on C-conversion and product distribution of cellulose gasification on (a) $Rh/CeO_2/SiO_2$ (35) and (b) G-91at 773 K. Cellulose feeding rate, 85 mg min^{-1} (C, 3148 μmol min^{-1}; H, 5245 μmol min^{-1} and O, 2622 μmol min^{-1}); air flow, 51 cm^3 min^{-1} (O_2, 417 μmol min^{-1}); N_2 flow 51 cm^3 min^{-1}.

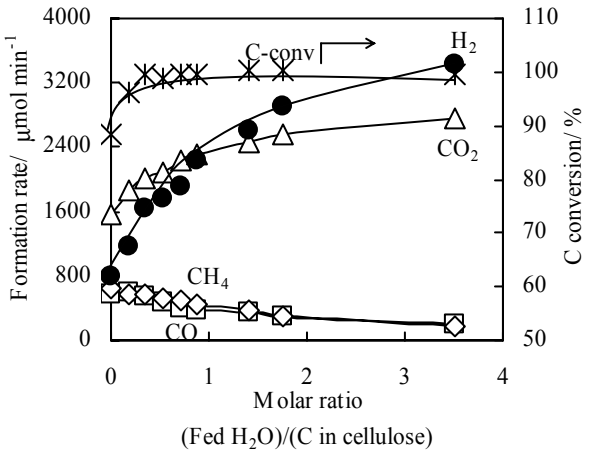

Figure 2. The influence of the steam to gas formation rate and C-conversion at 773 K over $Rh/CeO_2/SiO_2$ (35). Cellulose feeding rate, 85 mg min^{-1} (C, 3148 μmol min^{-1}; H, 5245 μmol min^{-1} and O,2622 μmol min^{-1}); air flow, 100 cm^3 min^{-1} (O_2, 818 μmol min^{-1}); N_2 flow 50 cm^3 min^{-1}(2046 μmol min^{-1}); H_2O, 555 ~11110 μmol min^{-1}.

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