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PRIORITY COMMUNICATION

Biomass Gasification to Hydrogen and Syngas at Low Temperature: Novel Catalytic System Using Fluidized-Bed Reactor

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We have developed a novel catalytic process for hydrogen and syngas production from biomass at very low temperature using an excellent catalyst ($Rh/CeO_2/SiO_2$) in a continuous-feeding fluidized-bed reactor using cellulose as a model compound. The catalyst simultaneously promoted the reforming and combustion reactions of pyrolyzed products of cellulose, such as tar, char, and so forth, and the water–gas shift reaction. In the presence of a mixture of air and steam, the cellulose completely converted to gas products at 773 K. This work can represent a new and energy efficient approach to the synthesis of hydrogen and syngas from biomass. © 2002 Elsevier Science (USA)

Key Words: **biomass gasification; catalytic gasification; hydrogen; syngas; fluidized-bed reactor.**

INTRODUCTION

Hydrogen is nowadays the most promising energy source that can be used in fuel cells and internal combustion engines. And it offers the large potential benefit of reducing emissions of pollutants and greenhouse gases (1–4), which are known to be derived from fossil fuel burning (5). The state-of-the-art of hydrogen production is the high-temperature steam reforming or the partial oxidation of fossil resources such as methane, light hydrocarbons, naphtha, and heavy oils (6–10). To meet the growing demand of hydrogen and to prevent any energy-related problems, alternative hydrogen sources, which should be renewable and sustainable, efficient and cost-effective, and convenient and safe, must be developed and the production method also must be energy efficient (11, 12).

A number of different ways of producing hydrogen from alternative sources have recently been investigated (13–20). However, hydrogen production from biomass holds the greatest promise (20, 21), since biomass is abundantly available everywhere in the world. Although biomass can be converted to hydrogen and syngas, the process is problematic because of the formation of tar (a complex mixture of higher hydrocarbons) and char even in the process operated at very high temperature (>1173 K). When the process is carried out at lower temperature (<1123 K) to get higher energy efficiency, more tar and char are produced. For example, a Ni catalyst for the hydrocarbon steam reforming was used in the secondary reactor for bio-oil reforming to hydrogen; however, the catalyst suddenly deactivated. Thus the process remains problematic (21).

Biomass gasification to produce hydrogen and/or syngas ($H_2 + CO$) has been considered to be a promising method for future energy systems to meet environmental requirements (1, 11, 21). However, the gasification needs complete conversion of the biomass to gas as well as high selectivity of the useful gas. Especially, a novel catalyst with high performance and a suitable reactor are necessary for a highly efficient low-temperature process. We have developed, and describe here, such a process for cellulose gasification using the $Rh/CeO_2/SiO_2$ catalyst in a continuous-feeding fluidized-bed reactor at temperatures as low as 773 K.

METHODS

A continuous-feeding fluidized-bed reactor system was used in this work. The experimental system is almost the same as a batch-feeding system previously described (22). However, the reactor dimensions and feeding system were modified for a continuous-feeding gasification system. Here the gasification reactor is a quartz tube 66 cm high, with a 1.8-cm i.d. The reactor consisted of a fluidized-bed section at the middle of the reactor. The cellulose feeder consisted of a glass vessel with a small pore, about 0.5 mm in diameter, at the bottom allowing continuous feeding from vibration of the vessel with a vibrator. The vibration rate controlled the feeding rate. Cellulose particles (Merck;

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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 bed temperatures at different points were measured by thermocouples. The sample of the product gas was collected from the sampling port by microsyringe and analyzed by gas chromatography (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 $Rh(C_5H_7O_2)_3$. After evaporating the acetone solvent, the catalyst was dried at 393 K for 12 h. The final catalyst was pressed, crushed, and sieved to 150- to 250-μm particle size. The loading amount of Rh was 1.2×10^{-4} mol (g of catalyst)$^{-1}$. The 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. The fresh (after H_2 treatment) and used catalysts were characterized by Brunauer–Emmett–Teller (BET) analysis and transmission electron microscopy (TEM). The TEM observation of the fresh and used catalysts was carried out by means of a JEM-2010F microscope (JEOL) operated at 200 kV. Samples were dispersed in tetrachloromethane by a supersonic wave and put on Cu grids for the TEM observation under air atmosphere. The methane combustion reaction was carried out on various catalysts within the temperature range of 523–1123 K using CH_4/air = 2/98 under atmospheric pressure. The 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 hydrogen treatment at 773 K for 0.5 h.

RESULTS AND DISCUSSION

Catalyst Development

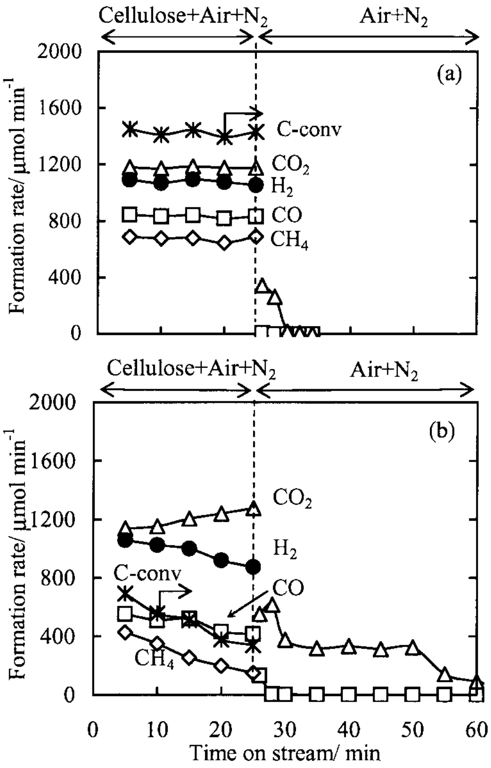

FIG. 1. Dependence of time on stream on C conversion and product distribution of cellulose gasification on (a) $Rh/CeO_2/SiO_2$ (35) and (b) G-91 at 773 K. Cellulose feeding rate, 85 mg min^{-1} (C, 3148 μmol min^{-1}; H, 5245 μmol min^{-1}; and O, 2622 μmol min^{-1}); air flow, 51 cm^3 min^{-1} (O_2,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

The results of the activity test of cellulose gasification over $Rh/CeO_2/SiO_2$ (35) and commercial steam reforming catalyst (G-91) at 773 K are shown in Fig. 1. On $Rh/CeO_2/SiO_2$ (35), the carbon conversion {C-conv = (formation rate of CO + CO_2 + CH_4)/(C feeding rate in cellulose) × 100} to gas and formation of H_2, CO, CH_4, and CO_2 was stable (Fig. 1a). In contrast, the C-conv decreased with time on stream on G-91 (Fig. 1b). The rest of the carbon corresponded 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. The figures clearly show that the deposited carbon on the G-91 catalyst is much higher than that of $Rh/CeO_2/SiO_2$ (35) catalyst. In this paper, the total amount of the CO_2 is assigned to the amount of char, as listed in Table 1. The char usually accumulates on the catalyst surface with lower activity and slowly takes part in the combustion reaction. Consequently, in the continuous-feeding system the amount of char gradually increases on the lower active catalyst surface 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 loadings of CeO_2 were prepared and tested in the gasification of cellulose in a continuous-feeding fluidized-bed reactor using air as a gasifying agent at 823 K. 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 (22), the Rh/CeO_2 catalyst exhibited considerably high C-conv; however, the BET surface area drastically

TABLE 1

Performance of Various Catalysts in the Gasification of Cellulose[a]

		Formation rate (μmol min^{-1})					C-conv[b]	Char[c]	Tar[d]
Catalyst	T (K)	CO	H_2	CH_4	CO_2	H_2/CO	(%)	(%)	(%)
$Rh/CeO_2/SiO_2$ (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	75	4	21
	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} × 100.

[c] Percentage char = ($CO + CO_2$ formation amount after stopping cellulose feeding/total C feeding) × 100.

[d] Percentage 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).

decreased after the reaction because of CeO_2 aggregation (23). 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 a decrease in surface area from 60 to 13 m^2 g^{-1}. The loading of CeO_2 on the high-surface-area SiO_2 inhibited the aggregation of CeO_2 and maintained the catalytic activity of $Rh/CeO_2/SiO_2$ (35). Among the various loadings, the 35 mass% of CeO_2 on SiO_2 totally is the most suitable support for Rh catalyst in terms of the C-conv, gas yield, and fast char conversion (Fig. 1a). In addition, no decrease in the BET surface area of this catalyst was observed. As shown in 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 approach the novelty of $Rh/CeO_2/SiO_2$ (35) catalyst for cellulose gasification.

Effect of the Temperature

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 noncatalytic gasification and pyrolysis are listed in Table 1. The C-conv as well as the CO and H_2 formation is the function of temperature and the catalyst activity. The increase in temperature favors the C-conv and syngas formation either in the catalytic or in the noncatalytic 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% of the carbon in the cellulose was converted to gas, with a considerably high yield of CO and H_2 at temperatures 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). Remarkably, methane was formed on the highly active $Rh/CeO_2/SiO_2$ (35) catalyst from the CO hydrogenation. On the other hand, the lower C-conv was achieved on the dolomite and in noncatalyst system even at 1173 K. Especially, in the noncatalytic 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 to the steam reforming of tar and char and the water–gas shift reactions ($H_2O + CO \rightarrow CO_2 + H_2$). The presence of steam in the reaction system facilitates the tar and char conversion to gas. Thus, in the next experiments, we added various amounts of steam.

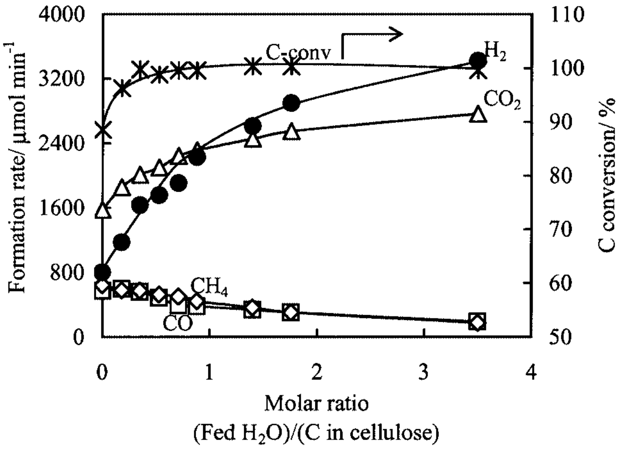

FIG. 2. The influence of the steam-to-gas-formation rate and C conversion in the gasification of cellulose at 773 K over $Rh/CeO_2/SiO_2$ (35). Cellulose feeding rate, 85 mg min^{-1} (C, 3148 μmol min^{-1}; H, 5245 μmol min^{-1}; and O, 2622 μmol min^{-1}); air flow, 100 cm^3 min^{-1} (O_2, 818 μmol min^{-1}); N_2 flow, 50 cm^3 min^{-1} (2046 μmol min^{-1}); and H_2O, 555–11,110 μmol min^{-1}.

Effect of the Steam

The C-conv as well as the selectivity of H_2 was dramatically improved by the steam addition (Fig. 2) in the gasification of cellulose on $Rh/CeO_2/SiO_2$ (35) catalyst. In the absence of steam, 86% C-conv with 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 an increase in 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 (24); however, in the primary-bed reactor the Ni-based catalysts suddenly deactivated as a result of carbon deposition (25, 26), and a similar phenomenon was observed for G-91.

The life of the $Rh/CeO_2/SiO_2$ (35) catalyst was tested at 823 K with a constant flow of the air and steam for 7 h. It was observed that in the experimental conditions used here, the C-conv and the product gas composition remained constant. Figure 3 shows the TEM images of $Rh/CeO_2/SiO_2$ (35) after H_2 reduction (Fig. 3a) and the reaction for 7 h (Fig. 3b). The BET surface area measurement and the TEM observation (Fig. 3b) of the used catalyst were carried out and almost no structural change was observed. This suggests that the catalyst activity can remain constant over a prolonged reaction time.

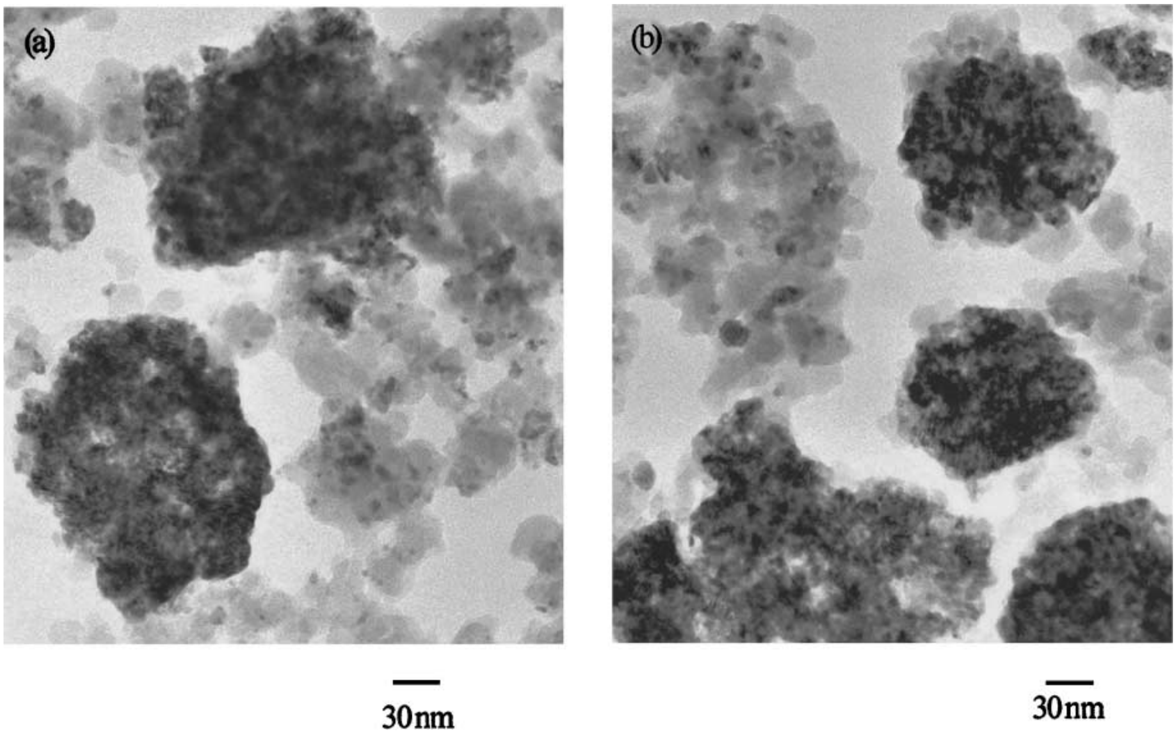

FIG. 3. TEM images of $Rh/CeO_2/SiO_2$ (35) after the reduction and the reaction. (a) Hydrogen reduction at 773 K for 0.5 h. (b) Cellulose gasification at 823 K for 7 h. Reaction conditions: cellulose feeding, 85 mg/min (C, 3148 μmol/min; H, 5246 μmol/min; O, 2624 μmol/min); air, 100 cm^3/min (O_2, 818 μmol/min); N_2, 50 cm^3/min; and H_2O, 4444 μmol/min.

Effect of the Catalyst Fluidization

It is thought that catalyst fluidization plays a major role in regenerating an active catalyst surface. In the feeding line, where the oxygen and external steam are absent, the cellulose is first pyrolyzed to tar, char, H_2O, and a small fraction of gas. Then all the products diffused into the catalyst bed, where the tar and char converted to gas during fluidization of catalyst. We think that the catalyst is oxidized and it can contribute to the combustion of the tar and char in the lower part of the bed since oxygen is available. In the upper part of the bed it can contribute to the reforming of the tar and char since oxygen is absent. Moreover, the steam directly takes part in the conversion of tar and char to gas as well as in the water–gas shift reaction on the catalyst surface. And thus 100% C-conv with a high yield of hydrogen even at the low temperature (773 K) becomes possible. Since the catalyst bed is in the fluidized condition, the catalyst particles can interact with the oxygen frequently at the lower part of the reactor. This can contribute to the removal of char with low reactivity by combustion (Fig. 1). Methane combustion activity has been tested and it was found that the $Rh/CeO_2/SiO_2$ (35) catalyst had much higher activity than that of Rh/CeO_2, Rh/SiO_2, and G-91 (Fig. 4). Furthermore, the temperature in the fluidized bed is usually homogeneous. In our fluidized reactor, the temperature difference between the lower and upper parts and also between the outside and inside of the reactor was found to be less significant (only 15 K). And a fluidized-bed reactor is more effective at removing the less reactive carbonaceous species (27, 28).

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 hydrogen and syngas production from biomass at low temperature with a high energy efficiency. In this communication, pure cellulose was used as the model compound of biomass. When we apply the catalyst to real biomass, it is expected that impurities such as sulfur and halogen will poison the catalyst. However, we think our catalytic process will have resistance to it. In the fluidized-bed reactor, the catalyst circulates in the oxidizing and reducing atmosphere. Under this condition, the surface of the active site can be kept clear by this *in situ* treatment. Therefore our catalytic process holds promise for the gasification of biomass with low levels of impurities, such as wood.

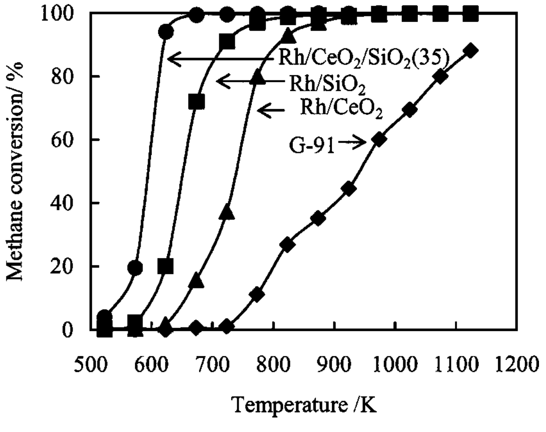

FIG. 4. Catalytic activity of methane combustion. Conditions: reaction temperature, 523–1123 K; CH_4/Air = 2/98; total pressure, 0.1 MPa; $W/F = 0.4$ g h^{-1} mol^{-1}; hydrogen pretreatment at 773 K for 0.5 h.

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