Highly Efficient Catalyst for Biomass Gasification to Produce Hydrogen and Syngas at Low Temperature

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Introduction

The greenhouse gases especially CO\textsubscript{2} and particulate matters, which cause of fear for us and our new generation are mainly coming from fossil fuel burning for energy purpose. To reduce emissions of pollutants and greenhouse gases, the future energy resources should be clean and carbon neutral or carbon balanced between resources and atmosphere.\textsuperscript{1-4} Hydrogen is one of the most promising energy source which offers no emission of particulates and greenhouse gases. 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.\textsuperscript{5-9} To achieve the goal, the sources of hydrogen should be renewable and sustainable, efficient and cost-effective, convenient and safe.\textsuperscript{10,11} Biomass can meet the demand of future energy source since it is renewable and abundantly available everywhere in the world. Hydrogen or syngas can be produced from the gasification of biomass. The traditional process of biomass gasification is problematic because of tar and char formation during the gasification process even at very 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. The catalytic gasification of biomass seems to be promising to reduce tar amount in the product gas even at low temperature, however, the traditional Ni based or dolomite catalysts hardly reduce the tar content in the product gas. These catalysts are suddenly deactivated in the in-bed reaction system due to deposition of carbon on the surface.\textsuperscript{12} Highly efficient catalyst and a suitable reactor are necessary to overcome the problems. Here we describe such a process for the cellulose gasification using the Rh/CeO\textsubscript{2}/SiO\textsubscript{2} catalyst in a continuous-feeding fluidized-bed reactor at as low as 773 K.

Experimental

A continuous-feeding fluidized-bed reactor was used for cellulose gasification. The operation system is almost the same as previously published\textsuperscript{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\textsubscript{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\textsubscript{2}, and CH\textsubscript{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\textsubscript{2}) formed after stopping the feed of cellulose under the air flowing at the reaction temperature.

CeO\textsubscript{2}/SiO\textsubscript{2} was prepared by the incipient wetness method using the aqueous solution of Ce(NH\textsubscript{4})\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} and SiO\textsubscript{2} (Aerosil, 380 m\textsuperscript{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\textsubscript{2}/SiO\textsubscript{2} by impregnation of the support with acetone solution of Rh(C\textsubscript{2}H\textsubscript{5}O\textsubscript{3})\textsubscript{3}. The final catalyst was pressed, crushed and sieved to 150-250 μm particle size. Loading amount of CeO\textsubscript{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\textsubscript{2}O\textsubscript{3}, 10-14 wt% CaO and 1.4-1.8 wt% K\textsubscript{2}O. The composition of the dolomite was 21.0 wt% MgO, 30.0 wt% CaO, 0.7 wt% SiO\textsubscript{2}, 0.1 wt% Fe\textsubscript{2}O\textsubscript{3} and 0.5 wt% Al\textsubscript{2}O\textsubscript{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

In this study, the catalytic and non-catalytic gasification of cellulose were carried out at different temperature in a continuous feeding fluidized-bed reactor. The summation of the formation rate of CO and hydrogen as well as the carbon conversion with respect to various temperatures are shown in Figure 1. The carbon conversion (C-conv = \{formation rate of CO + CO\textsubscript{2} + CH\textsubscript{4}\} / (C-feeding rate in cellulose) \times 100\textsuperscript{o}) to gas and the formation of H\textsubscript{2} + CO are reasonably increased with increasing temperature in all the reactions. However, these values on Rh/CeO\textsubscript{2}/SiO\textsubscript{2} (35) catalyst are much higher than on well known Ni-based catalyst (G-91) and dolomite. The C-conv (26%) and gas formation at lower temperature (823 K) are very low in non-catalytic systems. In this system, combustion reaction mainly proceeded to form CO\textsubscript{2} and H\textsubscript{2}O. Although CO was formed slightly, hydrogen was hardly formed in this reaction at 823 K. At higher temperature (1173 K), partial oxidation reaction proceeded and CO was formed remarkably. Maximum 92% carbon converted to gas at this high temperature. The white fume of tar was formed in the non-catalytic system and part of which condensed and deposited in the out flow line. The condensed tar some times blocked the gas flow line and this is one of the problems of non-catalytic gasification of biomass. In the presence of dolomite, the C-conv slightly improved, however, hydrogen formation improved remarkably. The figure shows that the G-91 catalyst worked better with respect to both C-conv and gas formation at low temperature. It gave 79% and 94% C-conv at 823 and 973 K, respectively. Interestingly enough, 86% C-conv was achieved at as low as 773 K and that was achieved to about 100% at 923 K on Rh/CeO\textsubscript{2}/SiO\textsubscript{2} (35) catalyst.

Figure 2 shows the C-conv and CO, H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} formation on Rh/CeO\textsubscript{2}/SiO\textsubscript{2} (35) (Figure 1a) and G-91 (Figure 1b) catalysts with respect to the time on stream. To investigate the catalyst activity the reactions were carried out until 25 minutes. Within the reaction period, the C-conv to gas and formation of H\textsubscript{2}, CO, CH\textsubscript{4} and CO\textsubscript{2} were stable on Rh/CeO\textsubscript{2}/SiO\textsubscript{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\textsubscript{2} and this was much higher in the case of G-91 catalyst than that of Rh/CeO\textsubscript{2}/SiO\textsubscript{2} (35). The reforming reaction usually proceeds on the clean surface of the catalyst. Since the deposited carbon on G-91 catalyst gradually covered the active sites, the reforming of tar gradually decreased with increasing reaction time and thus the formation of product gases decreased gradually.
Figure 1. Influence of temperature on the carbon conversion and CO + H$_2$ formation rate in the cellulose gasification on Rh/CeO$_2$/SiO$_2$ (35) (■, ●); G-91 (●, ◆); dolomite (●, ○); and non-catalyst (△, ◻). 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$^{-1}$.

The C-conv as well as the selectivity of H$_2$ was dramatically improved by the steam addition 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$_2$O/C = 0.35 was introduced. Furthermore, the formation of hydrogen and CO$_2$ expectedly increased with increasing the H$_2$O/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; however, in the primary-bed reactor the Ni-based catalysts suddenly deactivated by the carbon deposition, and the similar phenomenon was observed for G-91.

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 the water-gas shift reaction on the catalyst surface. And thus 100% C-conv with 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. 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 (Figure 3). Furthermore, the temperature in the fluidized-bed is usually homogeneous. In our fluidized-bed reactor, the temperature difference between the lower and upper parts and also between the out and insides of the reactor was found less significant (only 15 K).

Figure 2. 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$^{-1}$); N$_2$ flow 51 cm$^3$ min$^{-1}$.

Figure 3. Catalytic activity of various catalyst on methane combustion.
Conclusions

The combination of the Rh/CeO$_2$/SiO$_2$ (35) catalyst with the fluidized-bed reactor provided the novel system for the hydrogen and syngas production from biomass at low temperature with a high-energy efficiency. In the fluidized-bed reactor, the catalyst circulates in the oxidizing and reducing atmosphere. Under this situation, the surface of the active site can be kept clear by this in-situ treatment. Therefore our catalytic process is promising in the gasification of biomass with low level of impurities such as wood.

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References