Hydrogen production with a metal oxide catalyst in high pressure high temperature water

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Abstract. Hydrogen production from biomass was attempted in high pressure high temperature water at 573 K by adopting partial oxidation to increase the yield of H₂ via CO production in the presence of ZnO. The results revealed that an addition of H₂O₂ as an oxidant to the reaction of glucose and sugarcane bagasse brought about the trend of increasing the yields of H₂, CO, and CO₂. However, the sensitivity of H₂ yield on H₂O₂ amount was different from those of CO and CO₂, namely the excess amount of H₂O₂ tends to decrease the H₂ yield with giving a maximum at a certain H₂O₂ amount. These indicated that the controllability of partial oxidation would be a key factor for maximizing the H₂ yield through biomass conversion by partial oxidative gasification in high pressure high temperature water

1. Introduction
Hydrogen (H₂) is quite an important species for chemical synthesis and energy production. Biomass is a candidate of H₂ resources because of its sustainability. Among all biomass, plant biomass containing mostly cellulose is the highest amount of organic material on the earth. High gasification temperatures, above 800 K, for cellulose and glucose have been studied [1][2]. Although a lower temperature process for energy production is favorable because the generation of high temperature typically requires a lot of energy. Among the gasification processes, high-pressure water media including supercritical region is noticed to reduce gasification temperature of biomass [3]. Gasification of Glucose, the monomer unit of cellulose, in high temperature water has been studied to understand the reactivity of cellulose. [4] - [7]. One of serious problem of the low temperature gasification of glucose is the production of CH₄ by-product due to its thermodynamical favorability under these conditions [7].

Cortright et al. [6] reported that high-selective H₂ formation from biomass-derived hydrocarbons including glucose was achieved by addition of platinum catalyst (3% Pt/γ-Al₂O₃) in saturated high temperature water, namely HCW at 498 K and 538 K, using a flow apparatus. The glucose gasification efficiency at 125 h of reaction time (that is, weight hour space velocity, WHSV, is equal to 0.008 g-biomass/g-catalyst/h) at 498 K and 538 K were 50 % and 84 %, respectively. The H₂ yields at 498 K and that at 538 K were 50 and 60 % based on the starting glucose and CH₄ yield was always below 10 % (glucose basis). Thus, this is a quite high-selective H₂ formation technique at a low temperature.

They [6] considered the C-C bond in carbohydrates such as glucose is broken on the metal surface into CO and H₂ because carbon in the carbohydrates always had O and H atoms. Successively the product CO reacts with water to from CO₂ and H₂ (water-gas shift reaction). They also suggested that
the water-gas shift reaction proceeds on the metal surface. In this catalytic system, these reactions achieved high yield and selective H2 formation. However, due to the high activity of the metal surface, hydrogenation of CO2 into methane was also observed. Also undesirable compounds like alkane was also produced through homogeneous glucose reaction such as dehydrogenation at these conditions. In addition, more cost effective material such as transition metal and its oxide must be used for H2 production, because platinum is an expensive material.

Partial oxidation of organic compounds such as n-hexadecane (n-C16H34) and organosolv-lignin in supercritical water provided high yield of CO compared to without supercritical water [8][9]. H2 production increased by NaOH or ZrO2 catalyst. We reported that these catalysts promoted CO by partial oxidation that further reacted with water to form CO2 and H2. For the establishment of a green process, the usage of homogeneous alkali is not suitable due to the negative impact to the environment. On the other hand, heterogeneous catalyst is favored due to easy-recycle and no environmental impact. However, the catalytic activity of ZrO2 is still low. Therefore other materials must be considered for partial oxidative gasification of organics to CO and then water-gas shift reaction to the product H2 with high yield and high selectivity. Also, we must explore the optimum condition to H2 production at relatively low temperature of hot compressed water.

In this study, we demonstrate a new approach of biomass gasification to H2 using partial oxidation in high pressure high temperature water at low temperature (573 K). First, we examined the effect of a metal oxide (ZnO) on glucose reaction. Next, partial oxidation was employed for glucose/metal oxide/water system by focusing on H2 formation.

2. Experimental

Glucose was obtained from Wako Chemical and used without further purification. Sodium hydroxide (NaOH, 1 M aqueous solution) and sulfuric acid (H2SO4, 1 M aqueous solution) were purchased from Wako Pure Chemical and used as received. Hydrogen peroxide aqueous solution (ca. 30% H2O2 solution) was also obtained from Wako Pure Chemical. ZnO obtained from Wako Pure Chemical and used without pretreatment. Distilled water was obtained from a water distillation apparatus (Yamato Co., model WG-220).

The reaction was carried out in an SS 316 stainless steel tube bomb reactor with an inner volume of 6 cm3. One can see the detail experimental procedure elsewhere [9]. Briefly, the loaded amounts of glucose, water, and a metal oxide were 0.1 g, 1.0 g, and 0.1 g. In the case of adding homogeneous catalyst (NaOH or H2SO4) or liquid oxidant (H2O2), each aqueous solution prepared at a concentration was loaded into the reactor, instead of pure water. Ar gas was loaded at 25 MPa to recovery of gaseous product easily after the reaction. The reaction temperature was 573 K and the reaction time was 90 sec. The temperature profile in a batch type reactor was found elsewhere [11].

The identification and quantification of produced gas was conducted by GC-TCD (Shimadzu, model GC-7A, and Hitachi, model GC163). For recovering liquid and solid in the reactor, the reactor was washed with pure water. The amount of carbon (both inorganic and organic) in the water solution was evaluated using TOC (total organic carbon detector, Shimadzu, model TOC-5000A). The solid materials including the metal oxide catalyst and sometimes char) was divided by filtration with membrane filter.

Product yield (mol%) of carbon compound was evaluated from carbon base as shown below:

\[
\text{Product yield [mol%]} = \frac{\text{An amount of carbon atom in a product}}{\text{The amount of carbon atom in the loaded glucose}} \times 100 \quad (2.1)
\]

Hydrogen yield (H2 yield, mol%) was evaluated from hydrogen base of a loaded amount of samples as follows:

\[
\text{H2 Yield [mol%]} = \frac{\text{An amount of hydrogen atom in a produced H2}}{\text{The amount of hydrogen atom in the loaded glucose}} \times 100 \quad (2.2)
\]
In order to know how effective H$_2$ formed from glucose, we evaluated H$_2$ selectivity (HS) by following the method of Cortright et al. [6]. They evaluated the HS value by using the following equation (Eq. 3), to know how much hydrogen atoms in an organic compound can be taken out as H$_2$ [6]:

$$HS = \frac{H_2 \text{ produced, mol}}{C \text{ atom in gas phase}} \times 100$$

(2.3)

In the right hand side, they considered the H$_2$/CO$_2$ reforming ratio as 1/2. Glucose is represented as C$_6$H$_{12}$O$_6$ and thus maximum hydrogen will be 12H$_2$ corresponding to 6CO$_2$ (6CO form from glucose with 6H$_2$ and the product CO produces 6H$_2$ through water-gas shift reaction).

3. Results and Discussion

3.1.1. Without metal oxides. First we examined the gasification of glucose without metal oxide catalyst at 573 K. As reported elsewhere, the conversion in the heating period (within 90 sec) was about 95 % without catalyst. In this study, glucose completely converted at all the experiments and the gas products were only shown here because we focused on gas formation. One can see liquid product in this experimental condition without catalyst and with homogeneous catalysts (H$_2$SO$_4$ and NaOH) elsewhere [11][12].

Figure 1 shows the gaseous carbon product distribution without catalyst and with homogeneous catalysts (1mM H$_2$SO$_4$ and 1mM NaOH). Any hydrocarbon such as methane was not obtained. Only CO$_2$ formed without catalyst and only CO was produced with H$_2$SO$_4$. By adding NaOH, CO$_2$ formation was significantly enhanced and CO also formed. Figure 2 shows H$_2$ yield. In these cases, however, H$_2$ yield was always below 0.05 mol% with and without the homogeneous catalysts. The highest H$_2$ yield was obtained without catalyst. The differences among these H$_2$ yields in this scale are too low to argue the difference of the reaction behavior. Thus, H$_2$ production from glucose at 573 K and 90 sec is concluded to be quite low even in the presence of these homogeneous catalysts.

3.1.2. In the presence of ZnO. In order to enhance H$_2$ production, some metal oxides were examined. As a result, by adding ZnO, H$_2$ yield was relatively high (3.6 mol%) compared to that without metal.
ZnO. Although the HS (see (2.3)) with ZnO was high (22 %), the HS reported by Cortright et al. was much higher (36 %) [6] and the additional technique must be introduced.

In order to enhance the HS, C-C bond scission of glucose structure must be promoted and loosing of O and H atoms in the structure as H_2O must be inhibited because C-C bond scission produces CO and H_2. ZnO is known to be the catalyst of low temperature water-gas shift reaction [13]. If the water-gas shift reaction must rapidly occur on the ZnO surface, H_2 formation could be increased by enhancement of CO formation. Partial oxidation of an organic compound in high water density of supercritical water is favored to produce partial oxidation products including CO [14] – [17]. Therefore, in the glucose gasification, partial oxidation was employed to promote CO formation in the presence of ZnO.

Figures 3 show the O/C ratio dependence on the gaseous carbon compound and H_2 yield. The O/C ratio is the ratio of oxygen atom (can act as O_2) to carbon atom and this (in the loaded glucose) was 0.29 (1.6 % H_2O_2 solution in the reactor) or 0.53 (2.7 % H_2O_2 solution in the reactor). The yields of CO_2 and H_2 increased with increasing the O/C ratio. The yield of CO_2 drastically increased with the increase of O/C ratio. In contrast, H_2 yield gradually increased with the O/C ratio. Figure 4 shows the HS calculated by (2.3). The HS values at 0 and 0.29 of O/C ratios were both 22 %, however, that at 0.52 of O/C was 14 %. This means that higher value of O/C ratio promoted complete oxidation of organic carbon or CO into CO_2. Now selective CO formation from glucose with a catalyst is under investigation to promote H_2 formation.

**Conclusion**

In this study, we found that ZnO was effective for glucose gasification in hot compressed water. Combination of partial oxidation and ZnO addition to glucose-hot compressed water system was quite useful for H_2 production from glucose. In order to enhance H_2 yield and selectivity from glucose, the desired catalytic property and the optimum conditions must be determined.

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