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One-step production of CO- and CO_2-free hydrogen from biomass

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Abstract: The reaction between a biomass (cellulose, sucrose, glucose, starch, cotton, or Japanese paper) and NaOH in the presence of water vapor produced pure hydrogen without CO and CO_2 at temperatures in the range 473–623K. The addition of Ni/Al_2O_3 or Rh/Al_2O_3 catalyst to cellulose enhanced the production of hydrogen at <573 K. The reaction between cellulose and NaOH can be written as: $C_6H_{10}O_5 + 12NaOH + H_2O = 6Na_2CO_3 + 12H_2$. The reactivities of alkali metal hydroxides were: KOH > NaOH >> LiOH.

Keywords: hydrogen production; biomass; cellulose; alkali metal hydroxide

INTRODUCTION

Hydrogen is a clean fuel that emits no CO_2 when it is used in H_2-O_2 fuel cells. However, approximately 95% of hydrogen produced today comes from carbonaceous fossil resources which inevitably emit a huge quantity of CO_2 into the atmosphere. The production of hydrogen from water by solar- or wind-driven electrolysis and photo-biological water splitting are not competitive with the current processes due to the present-day high costs of renewable energy.[1–4] In contrast, the production of hydrogen from biomass is a more practical, viable and potentially carbon-neutral option.[5–7]

Biomass is a renewable energy resource derived from the carbonaceous waste of various human and natural activities. It is derived from numerous sources, including the byproducts from the timber industry, agricultural crops, raw materials from the forest, major parts of household waste, and wood. Biomass does not add carbon dioxide to the atmosphere as it absorbs the same amount of carbon in growing as it releases when consumed as a fuel. Biomass is an important source of energy and the most important fuel worldwide after coal, petroleum and natural gas. There are two predominant types of biomass: starch and lignocellulosics. Most of the biomass on earth is lignocellulosic, the most abundant component being cellulose.

Among various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) is the most suitable for portable, automobile and on-site applications due to low operational temperature, high power density, quick start-up and rapid response to local changes. However, the current technologies for the production and storage of hydrogen are still far from satisfactory from the point of view of energy density, safe handling, size of the system and the cost for the purification of hydrogen.[8–10] In order to broaden the choices of the resources and the basic technologies, an innovative method for the production of hydrogen without CO and CO_2 is strongly desired. CO strongly poisons the Pt-electrodes in PEMFCs and CO_2 is a well known greenhouse-effect gas.

Here we show a unique method for the synthesis of hydrogen without evolving CO and CO_2, operating at relatively low temperatures (<573 K). The new method is based on the reaction between a biomass (cellulose, sucrose, glucose, starch, cotton, or Japanese paper) and alkali metal hydroxides in the presence of water vapor.

EXPERIMENTAL

The experiments for the reactions of biomass, alkali metal hydroxide, and water vapor were performed by using a conventional mass-controlled gas flow system under atmospheric pressure. Prior to the experiments, a biomass was mixed uniformly with an aqueous solution of alkali metal hydroxide of 50 wt%. The mole ratio of the carbon (in the biomass and biomass components) and alkali metal hydroxide was adjusted to be 1.0:2.0. In the case of the reaction of cellulose in the presence of solid catalysts, the catalysts (0.18 g) were mixed thoroughly with cellulose (0.45 g). The mixture of biomass or biomass component (with or without solid catalysts) with alkali metal hydroxide was mounted on an alumina boat which was placed at the center in a cylindrical alumina-made reactor. Air

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in the reactor was first flushed out with an Ar flow. Then, water vapor (19.2 kPa) was carried with the Ar flow and contacted with the biomass sample with alkali metal hydroxide at room temperature before the reaction. The flow rates of water vapor and Ar were 9.4 and 40 cm^3 (STP) min^{-1}, respectively, under 101 kPa total pressure. The reactor was heated with an electric furnace. The temperature of the sample was monitored with a thermocouple and controlled within an error of ±1K. The temperature was raised linearly with the time on stream of water vapor and Ar mixture from 373 K to 773 K at a rate of 1.9 K min^{-1}. The analysis of the gaseous products was performed by gas chromatography at a time interval of 2–12 min. The total amount of hydrogen produced for each sample was evaluated from the integration of the area below the corresponding kinetic curve (see Figs 1–6).

RESULTS AND DISCUSSION

Cellulose, a main component of trees and plants, impregnated with an aqueous solution of sodium hydroxide (50 wt% conc) was mounted on an alumina boat that was placed in a cylindrical alumina reactor under a gas mixture of water vapor and Ar flow. The heat treatment (373–773K) of the cellulose sample with NaOH initiated the evolution of hydrogen. The temperature of the reactor was raised linearly (1.9 K min^{-1}) with the time on stream of the gas mixture. The rate of hydrogen formation showed several maxima as shown in Fig 1. The hydrogen formation terminated at *ca* 750 K. Temperatures above 623 K caused methane formation. Therefore, it is desirable to perform the reactions at <623 K.

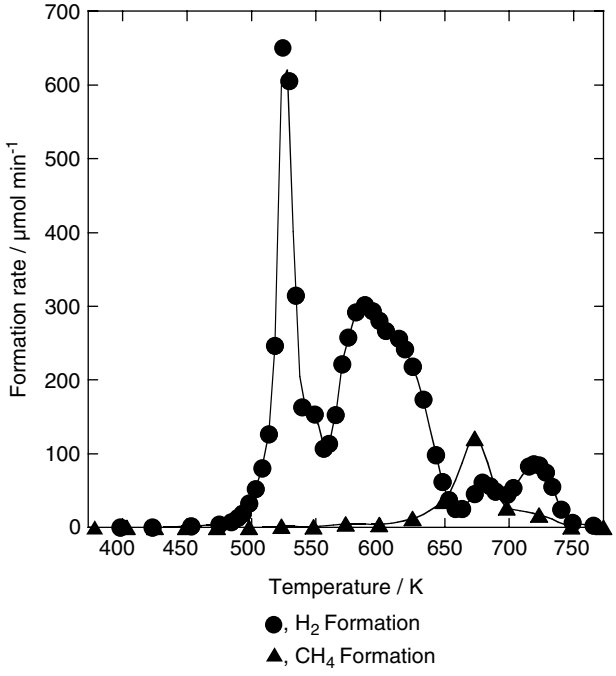

Figure 1. Hydrogen formation from the mixture of cellulose and NaOH. Temperature of the reactor was raised linearly from 373 K to 773 K with reaction time. Carrier gas: a mixture of Ar and water vapor (40.0: 9.4 cm^3 min^{-1}) under 101.3 kPa total pressure. Amounts of sample: NaOH (33.3 mmol), cellulose (0.450 g). The carbon content in the cellulose was 16.7 mmol.

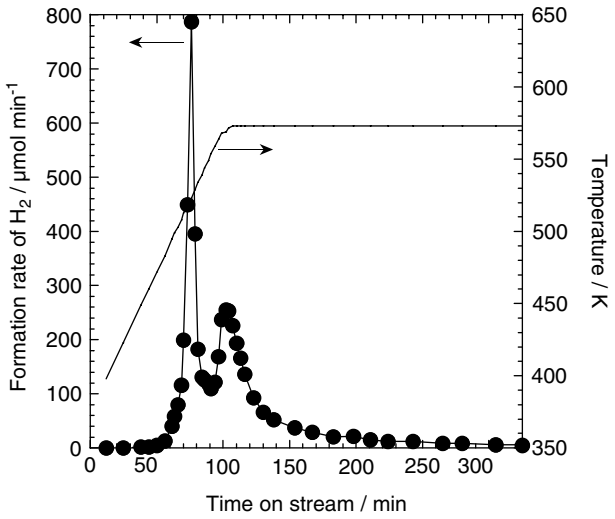

Figure 2. Hydrogen formation from the mixture of cellulose and NaOH. Temperature of the reactor was raised linearly from 373 K to 573 K with reaction time. The other experimental conditions were the same as those in Fig 1.

The results of the reaction of the same sample (cellulose + NaOH) at 573 K are shown in Fig 2. The temperature of the reaction was raised linearly with the time on stream of a mixture of water vapor and Ar from 373 K to 573 K in 107 min and was kept constant at 573 K afterwards. The total amount of hydrogen produced in 325 min was 6.84 mole per mole of the cellulose unit ($C_6H_{10}O_5$).

The results of the heat treatment (temperature was raised linearly with time from 373 K to 773 K) on the Japanese paper, cotton, sucrose, starch and glucose impregnated or absorbed with an aqueous solution of NaOH (50 wt% conc) are shown in Fig 3. The results of Japanese paper and cotton are quite similar to those of cellulose shown in Fig 1. Although the temperatures giving maximum rates of hydrogen formation were different between the substrates, it is generally concluded that pure hydrogen without CO, CO_2 and CH_4 could be obtained at <600 K for all the biomass materials shown in Fig 3.

The heat treatment of these biomass materials in the absence of alkali metal hydroxides caused the formation of CO and CO_2 as major gas products at 573–773 K with trace amounts of hydrogen and methane produced. Brown-colored oily products were also observed at the inner wall of the reactor exit. These unknown by-products were never observed for the samples impregnated with NaOH. The reaction between biomass and NaOH proceeded prior to the thermal decomposition of the biomass, selectively producing hydrogen at <573 K and hydrogen and methane at >573 K.

As examples, the reactions of cellulose[$(C_6H_{10}O_5)_n$], D-glucose($C_6H_{12}O_6$) and sucrose($C_{12}H_{22}O_{11}$)

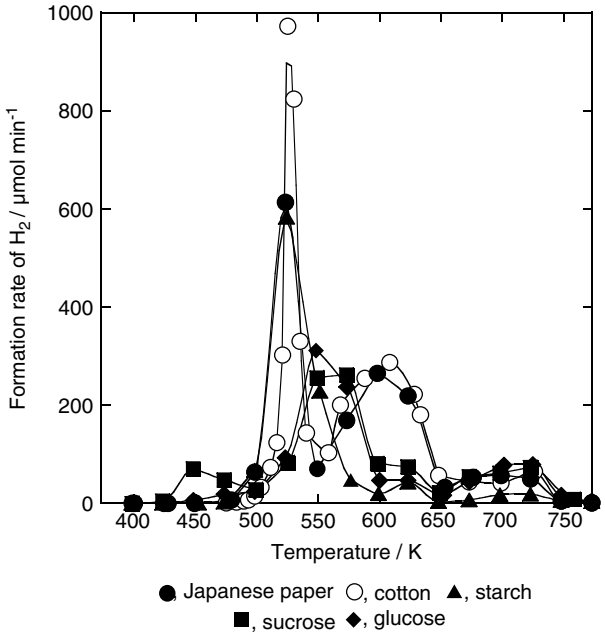

Figure 3. Hydrogen formation from the mixtures of biomass (Japanese paper, cotton, and starch) and NaOH or from those of biomass components (sucrose and glucose) and NaOH. Temperature of the reactor was raised linearly from 373 K to 873 K with reaction time. The other experimental conditions were the same as those in Fig 1.

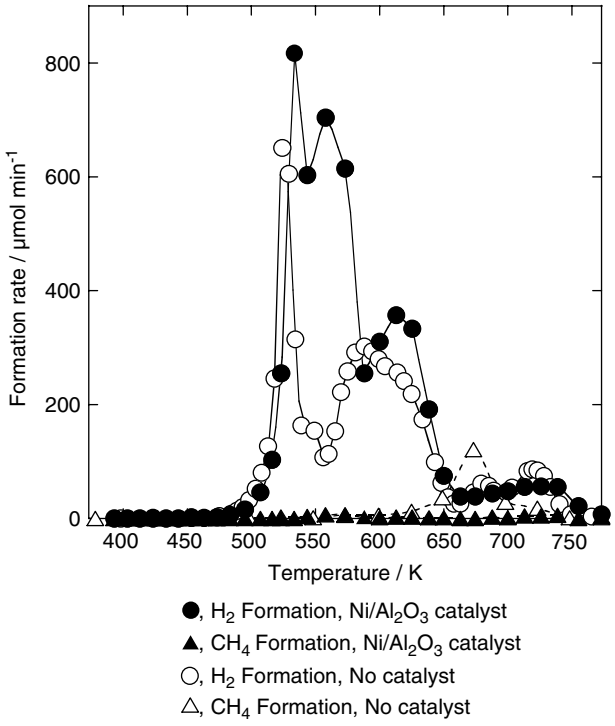

Figure 4. Effect of addition of Ni/Al_2O_3 on the hydrogen formation from the mixture of cellulose and NaOH. Weights of cellulose and catalyst were 0.45 and 0.18 g, respectively. Experimental conditions were same as those for Fig 1. For comparison, the rates of hydrogen and methane formation from Fig 1 are also shown.

with NaOH and H_2O may be written as follows:

$$C_6H_{10}O_5 + 12NaOH + H_2O = 6Na_2CO_3 + 12H_2 \quad (1)$$

$$C_6H_{12}O_6 + 12NaOH = 6Na_2CO_3 + 12H_2 \quad (2)$$

$$C_{12}H_{22}O_{11} + 24NaOH + H_2O = 12Na_2CO_3 + 24H_2 \quad (3)$$

The Gibbs free energy changes for the reactions of eqns (2) and (3) at 573 K are *ca* -1220 kJ mol-glucose^{-1} (-101 kJ mol-H_2^{-1}) and -2450 kJ mol-sucrose^{-1} (-102 kJ mol-H_2^{-1}), respectively.[11] Thus, the reactions of eqns (1), (2) and (3) are thermodynamically very feasible under the experimental conditions in this work.

The total yields of hydrogen produced through the reactions of cellulose, D-glucose, sucrose and starch with NaOH and H_2O, assuming eqns (1), (2) and (3), were *ca* 62%, 40%, 44% and 42%, respectively. However, when we added catalysts such as an alumina-supported Ni or Rh, the yield of hydrogen through the reaction of cellulose was dramatically improved. The results for the mixture of cellulose, NaOH and the alumina-supported Ni (Ni(20 wt%)/Al_2O_3) or Rh (Rh(20 wt%)/Al_2O_3) are shown in Figs 4 and 5, respectively. The weight ratio of cellulose and the catalyst was 2.5 (catalyst weight = 0.18 g). The results in the absence of catalysts (Fig 1) are also shown in Figs 4 and 5 for comparison. The results illustrated in Fig 4 show that the rate of hydrogen formation at 525–575 K was specifically enhanced by the addition of Ni(20 wt%)/Al_2O_3. Moreover, the formation of methane at >623 K was dramatically

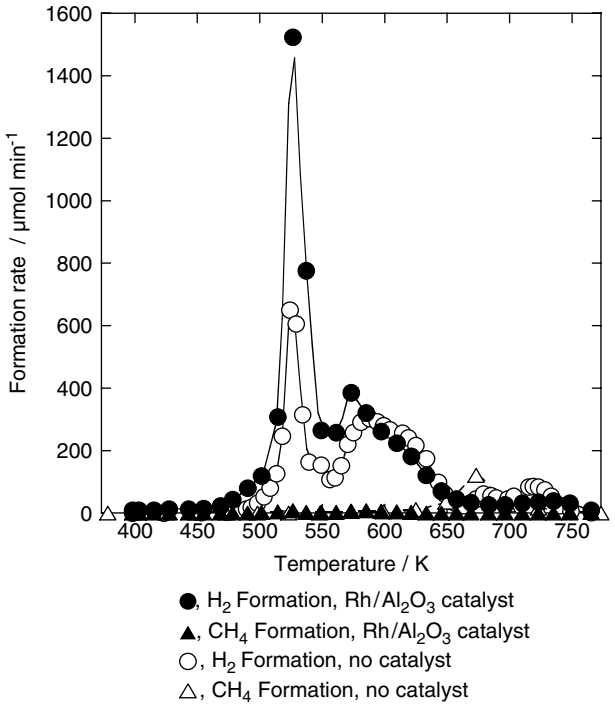

Figure 5. Effect of addition of Rh/Al_2O_3 on the hydrogen formation from the mixture of cellulose and NaOH. Weights of cellulose and catalyst were 0.45 and 0.18 g, respectively. Experimental conditions were same as those for Fig 1. For comparison, the rates of hydrogen and methane formation from Fig 1 are also shown.

suppressed by the addition of catalyst. In the case of Rh(20 wt%)/Al_2O_3 (Fig 5), the formation of hydrogen was enhanced especially at the low temperature range, 470–570 K. The formation of methane at >623 K was suppressed also by the addition of this catalyst to the mixture of cellulose and NaOH, as can be seen in Fig 5. The yields of hydrogen, assuming the stoichiometric reaction of eqn (1), were 98% and 102% for the results shown in Figs 4 and 5, respectively. The yields were almost 100% within the experimental error of ±5% in this work. This fact strongly supports that the reaction of cellulose occurs according to eqn (1).

Figure 6 shows the results of reactions of cellulose with KOH and LiOH under a flow of water vapor and Ar. If one compares these results with those in Fig 1, it is obvious that the formation of hydrogen at >*ca* 620 K was specifically enhanced by using KOH. The formation of methane was suppressed to some extent. The total yield of hydrogen produced from the mixture of cellulose and KOH was 78% assuming the similar reaction to eqn (1). The yield was improved by *ca* 16% by substituting NaOH with KOH. However, the use of LiOH instead of NaOH deteriorated the formation of hydrogen. The yield of hydrogen dropped to 8%. These observations indicate that the reactivities of alkali metal hydroxides for the generation of hydrogen without CO and CO_2 were KOH > NaOH>>LiOH.

As described earlier, PEMFCs dislike CO because it strongly poisons the electrocatalyst (Pt) of the cell at the anode. From this point of view, the hydrogen produced from a mixture of NaOH and biomass did not contain CO (<20 ppm, analysis limit in this work). The other advantages of our hydrogen production system are as follows: (1) biomass is very cheap, (2) neither CO, CO_2, NO_x nor SO_x was formed, (3) the by-products, Li_2CO_3, Na_2CO_3 and K_2CO_3, are stable, (4) the alkali metal carbonates are value-added compared with the corresponding alkali hydroxides.

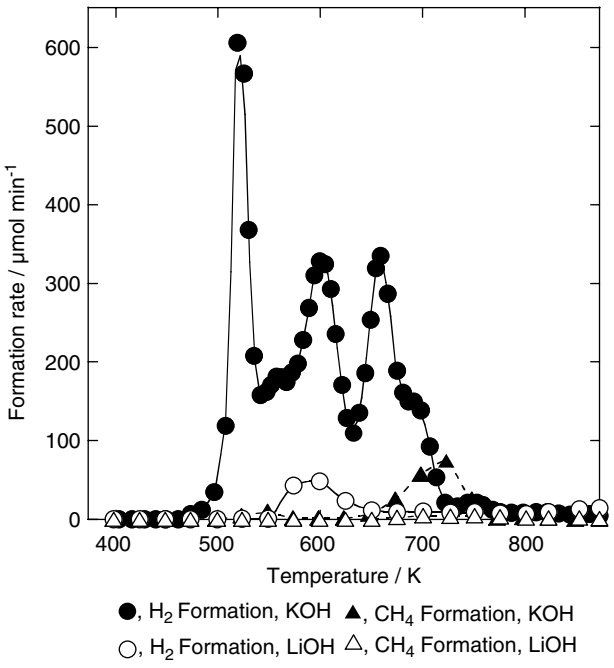

Figure 6. Hydrogen formation from the mixture of cellulose with KOH or LiOH. The amounts of alkali metal hydroxide were: LiOH(40.0 mmol), KOH(33.3 mmol). The other experimental conditions were same as those in Fig 1.

Detailed studies on the reaction mechanism and the role of catalysts in the reactions of cellulose, alkali metal hydroxides and water vapor will be reported in the near future.

CONCLUSION

One-step production of pure hydrogen without carbon oxides (CO, CO_2) was possible through the reaction of a biomass (cellulose, sucrose, glucose, starch, cotton, or Japanese paper) with NaOH and water vapor at temperatures 473–623K. The addition of solid catalysts such as Ni/Al_2O_3 and Rh/Al_2O_3 enhanced the reaction at <573 K. The reactivities of alkali metal hydroxides were: a KOH > NaOH>>LiOH. The method proposed in this work may be applicable for the supply of hydrogen to PEMFCs by using various biomass wastes without any purification treatment of the produced hydrogen.

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