Production of CO_x-free Hydrogen by Alkali Enhanced Hydrothermal Catalytic Reforming of Biomass-derived Alcohols

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CO_x-free hydrogen could be produced by hydrothermal catalytic reforming process when $Ca(OH)_2$ was added into the reaction, and biomass-derived alcohols were used as the reactants.

Hydrogen fuel cell attracted much interest of the world because it is environmentally clean[1] and high energy conversion efficiency.[2] It is very promising to be used in power generation, especially in electric automobile,[3] in the future. The production of hydrogen became more and more important for further application of hydrogen fuel cell. Current process for hydrogen production is mainly based on no-renewable fossil fuel resources and generated serious environmental pollution concerns at the same time.[4–7] Furthermore, hydrogen fuel cells are very sensitive towards CO_x impurities.[5] For example, the CO tolerance of proton exchange membrane fuel cells (PEMs) is only ppm level.[5] So the directly produced hydrogen from most current process can not be used for hydrogen fuel cells. It must be treated by several additional steps, such as water gas shift and preferential oxidation of CO processes etc., to remove CO_x impurities.[5] So it is very useful and economical to develop a clean, sustainable, and one-step CO_x-free hydrogen production method directly for hydrogen fuel cells, e.g., PEMs. In the past years, many efforts were made for producing clean hydrogen[8–11] or developing renewable ways for production of hydrogen.[12] Here, we report a simple, clean, and renewable method of alkali enhanced hydrothermal reforming of biomass-derived alcohols for production of CO_x-free hydrogen. The main product of this process is predominantly hydrogen. Little mount of alkanes was found in hydrogen product.

The hydrothermal reforming of alcohols was conducted in a homemade batch autoclave reactor. The reactor has 300 mL volume and can resist up to 220 atm pressures. 5 wt % Pt/AC (5 wt % Pt supported on active carbon) catalyst was used as reforming catalyst for the production of hydrogen. The hydrothermal reforming reaction of alcohols was carried at 533 K and autogenous pressure with continuous magnetic stirring. The gas products were analyzed by a Varian 3800 chromatograph with two detectors of FID and TCD and a mathanizer for conversion of low molar concentration of CO_x to methane then detected by FID. The quantity of gas product was measured by a wet gas flowmeter after the reaction finished. Reaction performance of alcohols such as methanol, ethylene glycol, glycerol, mannitol, and glucose were investigated in the experiments, separately. Calcium hydroxide ($Ca(OH)_2$) was used for enhancement of the hydrothermal reforming reaction of alcohols for its abundant resources. The detailed experiment data was shown in Table 1.

Alkali-enhanced hydrothermal reforming of alcohols keep most of advantages of aqueous reforming of alcohols:[12] The process was conducted under low temperature (around 500 K) and aqueous phase facilitated the water gas shift (WGS) reactions. Further more, addition of alkali ($Ca(OH)_2$) in the process could enhance the hydrogen production and suppress the CO_x concentration in the gas product. The ideal total reaction of aqueous reforming of alcohols for hydrogen production is listed as follows:

$$C_nH_xO_y + (2n - y)H_2O \rightarrow nCO_2 + (2n - y + x/2)H_2. \quad (1)$$

This reaction consists of the following two reactions:[12]

$$C_nH_xO_y + (n - y)H_2O \rightarrow nCO + (n - y + x/2)H_2, \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (3)$$

The reaction (2) is reforming process and (3) is water gas shift (WGS) process. However, in the real catalytic reactions, other reactions such as mathanation, Fischer–Tropsch etc. will take place.[12] So alkanes and oxygenated hydrocarbons will be produced beside the main products of hydrogen and CO_2.

When $Ca(OH)_2$ was added into the above process, the

Table 1. Detailed experiment data of alkali enhanced hydrothermal reforming of alcohols[a]

Experiment number	Polyols	Amount of alcohol/g	Amount of H_2O/g	Amount of $Ca(OH)_2$/g	Amount of catalyst/g
Exp.1	Glucose	6.0	90.0	15.0	1.2
Exp.2	Mannitol	6.0	90.0	16.0	1.0
Exp.3	Ethylene glycol	6.0	90.0	16.0	1.0
Exp.4	Glycerol	10.0	90.0	24.0	1.2
Exp.5	Glycerol	10.0	90.0	0	1.2
Exp.6	Methanol	6.5	90.0	16.0	1.0
Exp.7	Methanol	6.0	90.0	8.0	1.0
Exp.8	Methanol	6.1	90.0	4.0	1.0
Exp.9	Methanol	6.5	90.0	0	1.2

[a]Reaction conditions: temperature, 533 K; pressure, autogenous pressure; reaction time, 4 h.

Table 2. Composition of gas products of reactions

Experiment number	Polyols	Composition of gas products/mol %					
		H_2	CO_2	CO	CH_4	C_2H_6	C_3H_8
Exp.1	Glucose	81.9	0.0008	0.01	16.2	0.0	1.4
Exp.2	Mannitol	76.8	0.0	0.0001	18.2	3.6	1.5
Exp.3	Ethylene glycol	98.8	0.4	0.01	0.7	0.2	0.0
Exp.4	Glycerol	82.9	0.0006	0.0	16.4	0.6	0.2
Exp.5[a]	Glycerol	56.7	32.0	0.2	8.6	1.8	0.7
Exp.6	Methanol	99.9	0.001	0.00005	0.1	0.0	0.0
Exp.9[a]	Methanol	79.9	19.2	0.1	0.7	0.0	0.0

[a]Without addition of $Ca(OH)_2$.

following reaction may take place:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O. \quad (4)$$

The above reaction will push reactions (2) and (3) to move towards right hand, so the productions of CO_2 and H_2 were enhanced and the production of CO was suppressed theoretically. It was proved correct by the following reaction data of the experiments.

Table 2 shows the predominant gas products distributions. Other products such as alkanes and oxygenated hydrocarbons are ignored for their negligible amounts. From Table 2, we can see that the molar concentration of CO_x was very low in the gas products of all alcohols with the presence of $Ca(OH)_2$. However, the results were different with the different alcohols reactants. When mannitol acted as reactant, no CO_2 was detected in the gas product. Similarly, CO was not found in the gas product when glycerol was the reactant. The molar concentrations of CO_x in the gas products were relatively higher when glucose and ethylene glycol were used as reactants. In addition, when the reactants were glucose, mannitol, and glycerol, the molar concentration of methane was 16.2, 18.2, and 16.4%, respectively. The methane molar concentrations were relatively lower (<1%) when ethylene glycol and methanol were used as reactants. In general, the molar concentration of hydrogen in the gas product decreases in the order of methanol > ethylene glycol > glycerol > glucose > mannitol. The molar concentration of CO_x in the gas product could be suppressed to almost zero by addition of $Ca(OH)_2$.

The amounts of hydrogen produced by hydrothermal reforming of alcohols are shown in Table 3. The theoretical quantity of hydrogen produced according to reaction (1) is also listed in Table 3 for comparison. The hydrogen amount is expressed as volume at standard temperature and pressure (STP) per gram of alcohol reactant (L/g (alcohol)). The data shows that hydrogen quantity produced from real reactions is lower than theoretical calculation for all alcohols with the presence of $Ca(OH)_2$. The hydrogen production volume decreases in the order of ethylene glycol > methanol > glycerol > mannitol. It is worthy to notice that 1.7 liters hydrogen is produced per gram of ethylene glycol, which is slightly lower than the theoretical result 1.8 L/g (alcohol). When $Ca(OH)_2$ is absent, the reaction results of methanol and glycerol show that the hydrogen volume produced from the reactions decreased from 1.5 L/g (alcohol) and 0.7 L/g (alcohol) to 1.1 L/g (alcohol) and 0.39 L/g (alcohol), respectively.

Table 3. Amounts of hydrogen obtained from reactions and calculations

Experiment number	Polyols	STP[a] volume of hydrogen (L/g(alcohol))	
		Reaction	Calculation
Exp.2	Mannitol	0.62	1.6
Exp.3	Ethylene glycol	1.7	1.8
Exp.4	Glycerol	0.7	1.7
Exp.5[b]	Glycerol	0.39	1.7
Exp.6	Methanol	1.5	2.1
Exp.9[b]	Methanol	1.1	2.1

[a]Standard temperature and pressure. [b]Without addition of $Ca(OH)_2$.

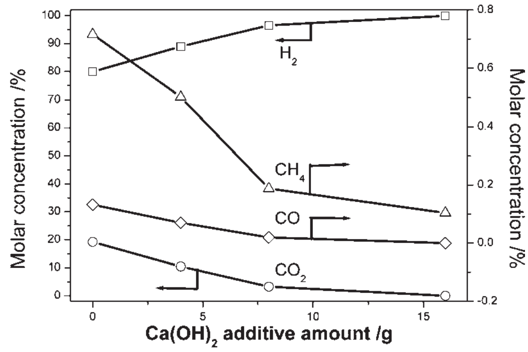

Figure 1. The composition of gas product as a function of $Ca(OH)_2$ quantity added into the reactions.

The effects of quantity of $Ca(OH)_2$ on the composition of gas product was investigated in the experiment, the results are shown in Figure 1. In this investigation, methanol was used as the reactant. Figure 1 shows the alkali amount has obvious effect on the molar concentrations of components in gas product, especially the CO_x concentrations. When additive amount of $Ca(OH)_2$ decreased gradually from 16.0 to 0 g, CO_2 molar concentration increased from ppm level to 19% step by step. The same as CO_2, molar concentration of CO increased from 0.5 ppm to 0.2%. Moreover, $Ca(OH)_2$ can also hold back the alkane production from the reforming reactions as shown in Figure 1.

All in all, by introducing alkali ($Ca(OH)_2$) into hydrothermal reforming reactions of alcohols, the CO_x, especially CO, in gas product can be suppressed to the utmost and reach several ppm or lower level. This is a simple one-step process for production CO_x-free hydrogen from renewable resources such as biomass-derived alcohols.

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Published on the web (Advance View) January 21, 2006; DOI 10.1246/cl.2006.216