



Direct conversion of cellulose into hydrogen by aqueous-phase reforming process

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ABSTRACT

Cellulose can be efficiently converted into hydrogen by an environmentally benign one-pot aqueous-phase reforming (APR) process over Pt/C catalyst. The hydrogen selectivity and yield were significantly higher than those for the glucose reforming and even comparable with those for the sorbitol reforming under similar conditions. It was found that this process involved the slow hydrolysis of cellulose to glucose and the subsequent rapid reforming of glucose to H₂. The relatively high efficiency for H₂ production was ascribed to the slow hydrolysis of cellulose, which was catalyzed by the H⁺ reversibly formed in water during the reaction.

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1. Introduction

Biomass is considered as an alternative to fossil fuels for sustainable production of hydrogen [1,2]. Among the various processes for the conversion of biomass into hydrogen, aqueous-phase reforming (APR) process was found to be an environmentally benign and efficient method for producing H₂ from biomass-derived polyols (e.g., ethylene glycol, glycerol and sorbitol) under mild conditions around 500 K [3]. Although these polyols could be readily produced from biomass via metal catalyzed hydrogenation and hydrogenolysis processes [4,5], the conversion of less reduced and more immediately available compounds such as glucose is more practical [3,6]. However, glucose tends to decompose in liquid phase, thus glucose is less reactive than polyols for APR [3,7]. Effort has been made by Davda et al. to convert glucose into hydrogen by combination of a hydrogenation reactor with a reforming reactor [7]. High hydrogen selectivity comparable with that for the reforming of polyol sorbitol could be obtained in their process.

Cellulose is the major component of biomass. Compared with the conversion of glucose, the direct conversion of cellulose is more practical. Herein, we report a novel one-pot process for the direct conversion of cellulose into hydrogen by APR reaction. It was noteworthy that the hydrogen selectivity and yield were significantly higher than those for the reforming of glucose and even also comparable with those for the reforming of sorbitol.

2. Experimental

2.1. Catalyst preparation

The precursors for the preparation of 5 wt.% Pt/C, 5 wt.% Pd/C, 5 wt.% Ir/C, 20 wt.% Ni/C and 20 wt.% Co/C catalysts were H₂PtCl₆, PdCl₂, H₂IrCl₆, Ni(NO₃)₂ and Co(NO₃)₂, respectively. These metal catalysts were prepared by HCHO reduction-precipitation method. Take the preparation of Pt/C catalyst for example, an aqueous solution containing the required amount of H₂PtCl₆, 5 wt.% NaOH aqueous solution and 38 wt.% HCHO aqueous solution were added dropwise into a powder activated carbon (Beijing Guanghua Jingke Activated Carbon Co., Ltd., GH-101) slurry in sequence under vigorous stirring, then heated in water bath for 1 h at 363 K. The as-prepared catalyst was filtered and washed several times with deionized water, and then dried at 383 K overnight.

2.2. Catalyst characterization

The catalyst characterizations were mainly focused on the most active and selective Pt catalyst. A NOVA-4000 physical adsorption instrument was used to measure the N₂ adsorption/desorption isotherms of the samples at 77 K. Prior to the measurements, the samples were degassed in vacuum at 553 K for 2 h to remove physically adsorbed components. The powder XRD patterns of the cellulose and catalyst samples were recorded on a PANalytical X'Pert PRO diffractometer fitted with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. Prior to the XRD test, the degreased cotton was crushed to powder. Transmission electron microscopy (TEM) measurements were carried out on a FEI Tecnai G² microscope.

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The mean size of the Pt particles and their size distribution were calculated by averaging of at least 200 particles randomly distributed in TEM images.

H₂ chemisorption measurement was carried out in a homemade setup equipped with a TCD detector. After being treated at 553 K in an Ar flow for 2 h, the catalyst sample was allowed to cool to room temperature for in situ chemisorption measurement. A spherical model for the metallic particles and an H:Pt stoichiometry of 1:1 were assumed in calculating metal dispersion and average particle size.

2.3. Catalytic activity test

Degreased cotton, filter paper and microcrystalline cellulose (Acros) were used as the cellulose materials, and the viscosity average degree of polymerization (DP) for these cellulose materials was 1203, 501 and 195, respectively. The reaction was conducted in a batch reactor described elsewhere [8]. In a typical experiment, 1.0 g powder catalyst, 90 g H₂O and feed were put inside the reactor. The autoclave was thoroughly purged with argon (initial pressure 0.1 MPa), and then heated to the desired temperature. The reaction time started after reaching the desired temperature. The heating rate was well reproduced in the experiments. When the reaction finished, the reactor was quenched by cold water. The quantity of gas product was measured by a wet gas flowmeter after the reaction was quenched to room temperature.

2.4. Product analysis

The gas products were analyzed according to the method described elsewhere [9]. The liquid effluent was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), total organic carbon (TOC), GC-MS (GC6890-MS5973 N, Agilent) and HPLC (Elite, RI detector, Sugar SC-1011 column (Shodex), mobile phase: water). The hydrogen selectivities are defined as the moles of H₂ produced normalized by the moles of H₂ that would be present if the carbon atoms detected in the effluent gas molecules had all participated in the reaction. Hydrocarbon selectivity is defined as the moles of carbon atoms in the gaseous hydrocarbon products normalized by the moles of carbon atoms in the effluent gas. The hydrogen yield is defined as the moles of hydrogen produced per gram of dry feed.

3. Results and discussion

The BET surface area, pore volume and mean pore size of the Pt/C catalyst were 873.4 m²/g, 0.095 cm³/g and 2.2 nm, respectively.

Table 1

Experimental results for APR of different cellulose materials, different concentrations of glucose and sorbitol.^a

| | Filter paper | Degreased cotton | Microcrystalline cellulose | Glucose | | | Sorbitol | |
|--|------------------|------------------|----------------------------|---------|-------|-------|----------|-------|
| Weight percentage (wt.%) | 2.2 | 2.2 | 2.2 | 0.3 | 0.5 | 2.4 | 9.1 | 2.4 |
| Conversion (%) | 100 ^b | 100 | 100 | 100 | 100 | 100 | 97.3 | 94.8 |
| Conversion of C to gas (%) | 70.4 | 82.6 | 89.8 | 56.2 | 59.9 | 64.7 | 18.1 | 76.4 |
| Gas-products composition | | | | | | | | |
| H ₂ (mol%) | 48.0 | 41.8 | 39.5 | 51.2 | 47.2 | 29.0 | 7.0 | 47.1 |
| CO ₂ (mol%) | 43.9 | 52.7 | 55.5 | 40.0 | 42.7 | 52.6 | 81.9 | 42.4 |
| CO (mol%) | 0.050 | 0.029 | 0.032 | 0.106 | 0.005 | 0.023 | 0.169 | 0.052 |
| CH ₄ (mol%) | 2.7 | 1.8 | 1.9 | 4.2 | 3.5 | 4.6 | 2.3 | 4.2 |
| C ₂ –C ₆ hydrocarbons (mol%) | 5.4 | 3.7 | 3.1 | 4.5 | 6.6 | 13.8 | 8.6 | 6.3 |
| H ₂ selectivity (%) ^c | 39.0 | 32.1 | 29.5 | 44.9 | 35.6 | 13.9 | 3.1 | 35.4 |
| Hydrocarbon selectivity (%) ^d | 28.7 | 19.0 | 16.9 | 29.6 | 35.5 | 49.8 | 26.6 | 36.2 |
| H ₂ yield (mmol/g) ^e | 20.3 | 19.7 | 19.6 | 17.0 | 14.4 | 6.0 | 0.4 | 17.9 |

^a Reaction conditions: *T* = 533 K, autogenous pressure, Pt/C powder catalyst 1.0 g, 4 h.

^b Cellulose conversion was calculated by the change in the weight of solid loaded before and after the reaction.

^c H₂ selectivity = (moles of H₂ produced/moles of C atoms in gas phase)/(1/RR) × 100, where RR is the H₂/CO₂ stoichiometric ratio in the ideal total reaction equation for the APR of the reactant compound [3]. RR values for the compounds are cellulose, 2; glucose, 2; sorbitol, 13/6.

^d Hydrocarbon selectivity = (moles of C atoms in gaseous hydrocarbons/total moles of C atoms in gas phase products) × 100.

^e H₂ yield = moles of H₂ produced/dry weight of feed.

The metal dispersion of the Pt/C catalyst was 78.7%, and the average Pt particle size calculated from the metal dispersion was 1.44 nm.

The experimental results for APR of different cellulose materials, different concentrations of glucose and sorbitol were summarized in Table 1. It can be seen from the table that the hydrogen selectivity for the cellulose reforming decreased from 39.0% to 29.5% in the order of filter paper, degreased cotton and microcrystalline cellulose. Filter paper gave the highest hydrogen yield of 20.3 mmol/g (equivalent to 0.04 g hydrogen per gram of cellulose), which is significantly higher than that of the unique process for the biomass conversion via APR process developed by Valenzuela et al. (0.96 mmol/g_{biomass}) [10]. It was noteworthy that the hydrogen selectivity and yield for the reforming of cellulose filter paper were also significantly higher than those for the glucose reforming even comparable with those for the sorbitol reforming at similar reactant content.

The structure of these cellulose materials was determined by XRD characterization (Fig. 1). As depicted in the figure, all samples showed native cellulose I structure, which typical diffraction peaks were centered around 14.8°, 16.3° and 22.6° [11]. The intensities of these peaks decreased in the following order of filter paper, degreased cotton and microcrystalline cellulose, indicating that filter paper has the highest degree of crystallinity, whereas microcrystalline cellulose has the lowest degree of crystallinity. It should be noted that the hydrogen selectivity decreased in the same order of cellulose materials as the degree of crystallinity decreased, hence it seemed that high degree of crystallinity would lead to high hydrogen selectivity. However, this order of the cellulose materials is not related to their degree of polymerization, thus it was likely that the degree of polymerization for these cellulose materials had minor effect on the hydrogen selectivity.

The degree of crystallinity is known to correlate with the hydrolysis rate of cellulose, as high degree of crystallinity would lead to slow hydrolysis of cellulose [12,13]. The hydrolysis step in our process was likely to be catalyzed by the H⁺ from the self-ionization of water in the absence of added acid catalysts under the APR reaction conditions around 500 K [14], similar to the direct hydrogenation of cellulose to form polyols [15,16]. As the monomer of cellulose, glucose is generally considered to be the key intermediate for the cellulose conversion under hydrothermal conditions [15–17]. In the case of glucose reforming, it can be seen from Table 1 that the hydrogen selectivity and yield decreased with the increase in glucose concentration. It was noteworthy that the reforming of cellulose filter paper gave similar gas distribution to the reforming of much lower concentration of glucose such as 0.3 wt.% and 0.5 wt.%.

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