

## Selective Hydrogen Production from Cellulose at Low Temperature Catalyzed by Supported Group 10 Metal

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Cellulose, a major component of woody biomass, reacts in hot-compressed water at 350 °C and 160–200 atm in the presence of a supported group 10 metal catalyst (2 wt%) for 10 min to give gas, consisting of hydrogen, carbon dioxide, and methane. Hydrogen was produced in high yield (8.1 mmol/g cellulose) and high selectivity ( $H_2/CH_4 = ca. 6$ ) catalyzed by a supported Ni, Pd, or Pt. Among them, Pd supported on  $Al_2O_3$  particularly had highest catalytic activity for this gasification.

Biomass is recognized as a promising and rich source of renewable energy.<sup>1</sup> Some groups recently reported wet biomass being directly gasified into methane, hydrogen, carbon dioxide, etc., promoted by late transition metals. Kawai et al. reported the gasification of cellulose in the presence of water vapor to form hydrogen, carbon monoxide, and carbon dioxide catalyzed by ruthenium, nickel, or platinum.<sup>2</sup> Elliott et al. treated various wastes and model compounds using a hot compressed water (200 atm, 350 °C) to mainly yield methane and carbon dioxide promoted by reduced nickel.<sup>3</sup> A pressurized catalytic gasification process operated at low temperature (350–450 °C) is effective for treating wet biomass for both environmental preservation and energy recovery. We have already reported that hydrogen and methane were mainly produced from wet cellulose or a microalga chlorella, by the gasification at lower temperature.<sup>3</sup> However, a large amount of late

transition metals as the catalyst (>20 wt%) is required for the gasification in previous research.<sup>1–4</sup> The gasification of wet biomass promoted by a small amount of catalyst is so noteworthy that we searched suitable catalyst for gasification. In this paper, we report that a supported group 10 metal acts as a highly active catalyst (2 wt%) for the gasification of cellulose to selectively produce hydrogen.

Cellulose, a major component of woody biomass, was used as the starting material. The cellulose sample was microcrystalline (E. Merck), and it was dried at 105 °C prior to use. The reaction was performed in a stainless steel autoclave (100 mL) with a magnetic stirrer. Water (30 mL), cellulose (5.002–5.067 g), and catalyst (0.05–0.1 g equivalent metal) were charged into the autoclave. Nitrogen gas was used to purge the residual air in the autoclave, and it was pressurized to 30.0–30.3 atm to avoid vaporization of the water during the reaction. The reaction was started by heating the autoclave to 350 °C using an electric furnace. The reaction temperature was kept at 350 °C for 10 min, then the autoclave was cooled to room temperature using an electric fan. The reaction products were gas, an aqueous phase (water-soluble), oil (water-insoluble, acetone-soluble), and char (water- and acetone-insoluble). The evolved gas was collected in a gas bag to measure the volume with a gas meter (Shinagawa Seiki, W-NK-0.5Bf) and its composition was analyzed by a gas chromatograph (Shimadzu, GC 12A) equipped with a thermal conductivity detector and a

**Table 1.** Gasification of cellulose at 350 °C catalyzed by supported late transition metal catalyst

Run	Catalyst	Weight Metal equivalent /g to cellulose/wt%	Holding time at 350 °C/min	$H_2$ /vol% /mmol	$CH_4$ /vol% /mmol	$CO_2$ /vol% /mmol	Gas /w%/cellulose	aqueous phase <sup>a</sup> %/C
1	reduced Ni	2.0	40	7.6 9.8	43.5 58.8	48.9 66.2	77.3	17.7
2	65 wt% Ni on $SiO_2/Al_2O_3$	2.0	2	34.3 17.6	6.3 3.23	59.4 30.5	28.2	62.9
3	5 wt% Pd on $Al_2O_3$	0.15	2	47.0 43.0	8.3 7.63	44.7 41.1	40.3	50.2
4	5 wt% Pd on activated carbon	2.0	2	34.0 11.9	19.7 6.90	46.3 16.2	16.9	26.1
5	5 wt% Pd on $CaCO_3$	2.0	2	41.2 19.9	5.4 2.61	53.3 25.7	24.2	61.2
6	5 wt% Pd on $BaCO_3$	2.0	2	29.6 10.0	0.49 0.165	69.9 23.6	21.0	36.1
7	5 wt% Pd on $ZrO_2$	2.0	2	20.4 3.94	5.2 1.00	74.4 14.4	13.1	60.5
8	1 wt% Pd on $Al_2O_3$	10	2	40.4 38.9	14.2 13.7	45.4 43.6	44.3	11.9
9	5 wt% Pd on $Al_2O_3$	1.0	1	17.1 6.54	34.8 13.3	48.1 18.4	18.8	54.3
10	5 wt% Pd on $Al_2O_3$	1.0	1	42.3 37.3	7.7 6.82	49.9 43.9	42.3	39.1
11	5 wt% Pt on $Al_2O_3$	2.0	2	31.3 20.9	9.2 6.14	59.5 39.8	37.7	48.7
12	1 wt% Pt on carbon	10	2	36.5 36.5	6.9 6.91	56.6 56.6	52.8	13.6
13	10 wt% Pt on activated carbon	1.0	2	36.0 33.8	7.3 6.83	56.7 53.1	50.2	28.3

Conditions: cellulose; 5.002–5.067 g,  $H_2O$ ; 30 ml, initial pressure;  $N_2$  30.0–30.3 atm.

<sup>a</sup>Carbon percentage in the aqueous phase to cellulose.

packed column (porapak Q). The aqueous phase was separated from the water-insoluble materials by filtration. The amount of carbon in the aqueous phase was determined using a total organic carbon meter (Yanaco, TOC-8L). The remaining material in the autoclave was a mixture of oil and char. As for the remaining products, that is, oil and char, this paper does not describe these by-products because their yields were quite small and negligible.

The results of the gasification of cellulose are summarized in Table 1. Most of the gasification was attempted using a supported late transition metal, mainly a group 10 metal as the catalyst in this paper. Reduced nickel acts as a promoter for the gasification from biomass as we previously reported.<sup>3</sup> Conversion yield is defined as weight percentage of cellulose converted hydrogen, methane, and carbon monoxide. In run 1, when using reduced nickel 40 wt% to cellulose, the gasification proceeded with a 77% conversion yield and methane was produced in high yield. The catalytic amount was 40 wt% to cellulose. In run 2, supported nickel on SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was used as a catalyst and the catalytic amount was dramatically decreased to 2 wt%. The amount of gas was less than that promoted by the reduced nickel, but hydrogen was produced in high yield. The gas consisted of 34 vol% hydrogen, 6 vol% methane, and 60 vol% carbon dioxide. On the other hand, supported palladium on Al<sub>2</sub>O<sub>3</sub> (run 3, 2 wt%) produced a much larger amount of gas, especially amount of hydrogen, than the reduced nickel. The volume ratio of hydrogen (47 vol%) was about 6 times higher than that of methane (8 vol%). Various palladium catalysts supported on Al<sub>2</sub>O<sub>3</sub> (run 3), activated carbon (run 4), CaCO<sub>3</sub> (run 5), BaCO<sub>3</sub> (run 6), or ZrO<sub>2</sub> (run 7) were examined. Among of them, Al<sub>2</sub>O<sub>3</sub> was the best palladium support for this gasification of cellulose. The catalytic activity did not dramatically change using the supported ratios of palladium on Al<sub>2</sub>O<sub>3</sub>, of 1 wt% (run 8) or 5 wt% (run 3). The catalytic activity was reduced as the amount of catalyst decreased (run 9), although the activity could be recovered by a longer reaction time, for example, 180 minutes in run 10. Moreover, the supported platinum works as a catalyst for the gasification (runs 11-13). The catalytic activity of platinum for the gasification was similar for that of palladium.

A few amount of oil and char were produced from these reactions described in Table 1, which does not prevent from the

catalytic gasification. Palladium supported on an Al<sub>2</sub>O<sub>3</sub> catalyst, 2 wt% to cellulose was recycled 5 times (shown in Table 2). Hydrogen, methane, and carbon dioxide generated mostly same volume and ratio for each reaction. This means that this gasification catalyzed by supported palladium catalyst can be expected to be used in a circulation system.

The gasification of cellulose has been tried using other late transition metal complexes or divalent group 10 metal complexes as a catalyst (ca. 2 wt% equivalent metal), such as Zr(OH)<sub>4</sub>, (CH<sub>3</sub>COCH=C(O-)CH<sub>3</sub>)<sub>3</sub>Fe, FeCp<sub>2</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, (CH<sub>3</sub>COCH=C(O-)CH<sub>3</sub>)<sub>2</sub>Co, NiC<sub>2</sub>O<sub>4</sub>, NiO, Ni(OH)<sub>2</sub>, 2NiCO<sub>3</sub>, 3Ni(OH)<sub>2</sub>, PdI<sub>2</sub>, CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>, (CH<sub>3</sub>CO)<sub>2</sub>Cu·H<sub>2</sub>O, (CH<sub>3</sub>COCH=C(O-)CH<sub>3</sub>)<sub>2</sub>Cu, and Cu(OH)<sub>2</sub>, though not gas, but oil and char were mainly produced from these reactions. This indicates that a supported zero valent group 10 metal acts as a good catalyst for the gasification of cellulose. It has already been clarified that C2-C10 unit aldehydes, ketones, and organic acids were formed from cellulose at 250 °C in hot compressed water (initial N<sub>2</sub> pressure: 30 atm) and then decomposed to give gas consisting of hydrogen, methane, carbon monoxide, and carbon dioxide promoted by the late transition metal.<sup>3</sup> These organic products might interact with the zero valent group 10 metal to cleave various bonds. Detail mechanistic study is now in progress.

The amount of total carbon in the aqueous phase was defined as carbon percentage of cellulose. This shows that products containing carbon from cellulose, such as esters, ketones, aldehydes, and alcohols, exist in the aqueous phase. Cellulose was mainly converted and distributed to gas and water-soluble organic products. This implies that catalyst could be easily separated from products and solvent to be available to recycle.

In this study, we found that hydrogen could be specifically obtained from wet biomass at the low reaction temperature of 350 °C by catalytic gasification using a supported zero valent group 10 metal. Hydrogen is a clean and valuable energy and chemical resource. This gasification would be expected to be one of the hydrogen production methods.

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**Table 2.** Recycle of palladium catalyst for the gasification of cellulose

Run	H <sub>2</sub> /vol% /mmol	CH <sub>4</sub> /vol% /mmol	CO <sub>2</sub> /vol% /mmol	Gas /w%/cellulose
1	47.0	8.3	44.7	40.3
	43.0	7.63	41.1	
2	46.1	8.2	45.7	41.1
	42.5	7.59	42.1	
3	46.9	7.6	45.5	38.5
	41.3	6.69	40.0	
4	46.6	7.8	45.6	39.9
	42.0	7.01	41.1	
5	43.9	7.4	42.9	38.5
	40.5	6.83	39.6	

Conditions: catalyst; 5 wt% Pd on Al<sub>2</sub>O<sub>3</sub>, metal equivalent to cellulose; 2.0, cellulose; 5.002-5.067 g, H<sub>2</sub>O; 30 ml, initial pressure; N<sub>2</sub> 30.0-30.3 atm, holding time at 350 °C; 10 min.