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Pentose Acting as a Sacrificial Multielectron Source in Photocatalytic Hydrogen Evolution from Water by Pt-doped TiO_2

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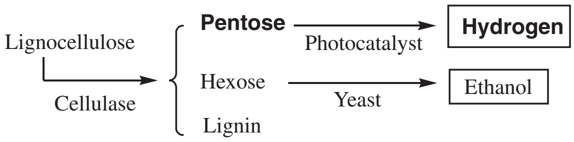
Photocatalytic reaction was performed by irradiation of Pt-doped TiO_2 in an aqueous solution of xylose acting as a sacrificial reagent to evolve hydrogen, whose amounts reached 8.6 equivalents to the xylose used.

Biofuel has been receiving a great amount of interest from the standpoint of utilization as a renewable resource.[1] However, commercially available bio-ethanol has been prepared from the starch of maize, sugarcane, and sugar sorghum, which are in competition with food sources for human consumption.[2] Therefore, we are interested in herbaceous cellulosic biomass such as napier grass and silver grass which is not in competition with food sources.[3] Recently we have reported the production of bio-ethanol from napier grass (*Pennisetum purpureum* Schumach) through enzymatic saccharification and fermentation with yeast (*Saccharomyces cerevisiae*). In this process, 8.8 g of ethanol was produced from 100 g of napier grass containing 44 g of cellulosic components.[4] Thus, ethanol yield was low because of high content of hemicellulose (20–35 wt %) composed of pentose, which cannot be fermented to ethanol by yeast. Therefore, the transformation of pentose to biofuel is highly desirable in the lignocellulosic biomass conversion (Scheme 1).

The first approach of photocatalytic conversion from carbohydrate to hydrogen has been reported by Kawai et al.[5] Recently, it was reported that Pt-doped TiO_2 (Pt/TiO_2) can catalyze photochemical H_2 evolution using a hexose as a sacrificial reagent according to eq 1.[6] Therefore, it is expected that this reaction can be applied to pentose (eq 2). Here, we examined the conversion from pentose to hydrogen by photocatalytic reaction with the Pt/TiO_2 in order to develop a methodology to produce biofuels from cellulosic materials efficiently.

$$C_6H_{12}O_6 + 6H_2O \xrightarrow[Pt/TiO_2]{h\nu} 6CO_2 + 12H_2 \quad (1)$$

$$C_5H_{10}O_5 + 5H_2O \xrightarrow[Pt/TiO_2]{h\nu} 5CO_2 + 10H_2 \quad (2)$$



Scheme 1. Biofuels production from lignocellulose.

The photocatalytic H_2 evolution was performed using a Pt/TiO_2 catalyst which contained 2 wt % of Pt.[7] The Pt/TiO_2 and an aqueous solution of xylose (**1a**, $C_5H_{10}O_5$) were introduced to a reaction vessel. The volume of reaction solution was adjusted to 150 mL with water. A high-pressure mercury lamp (100 W, UVL-100HA, Riko, Japan) was inserted into the reaction vessel which was connected to a measuring cylinder. The evolved gas was collected by a measuring cylinder and was analyzed by GLC.[8] The reaction vessel was purged by N_2 gas and was set in a water bath to keep at a constant temperature (usually 20 °C).

Irradiation was performed with a high-pressure mercury lamp under vigorous stirring with a magnetic stirrer until the gas evolution stopped. In order to efficiently irradiate the Pt/TiO_2 suspended in solution, the amount of the Pt/TiO_2 was optimized using **1a** (150 mg) (Table 1, Runs 1–4). When 100 mg of the Pt/TiO_2 was used in an aqueous solution (150 mL), the largest amount of H_2 was evolved. In the absence of the sacrificial reagent, the hydrogen evolution from water by irradiation of Pt/TiO_2 was small (Run 5). The photocatalytic reaction was performed for an aqueous suspension (150 mL) of the Pt/TiO_2 (100 mg) with varying amounts of **1a** (38–188 mg) (Runs 6–9). The molar ratio of the evolved H_2 to **1a** is plotted against the weight ratio of **1a** to the catalyst in Figure 1. As **1a**/catalyst decreased, the H_2/**1a** values increased. The intercept of the plots represents the limiting quantity of hydrogen (N) obtained from one mole of **1a**. The N value was 8.6 and did not reach 10 which is the maximum value (N_{max}) when pentose will be completely decomposed according to eq 2. This suggested that the complete decomposition of **1a** into CO_2 and water did not occur. Therefore, the decomposition procedure of **1a** was examined.

Charge separation of TiO_2 by photoexcitation is well-known to be responsible for the initiation step of the present photocatalytic reaction.[9] The electron reduced water to generate H_2 (eq 3). The hole (h^+) oxidizes HO^- rather than **1**, because of the low concentration of **1** (eq 4).

$$TiO_2 \xrightarrow{4h\nu} 4e^- + 4h^+ \left\{ \begin{array}{ll} 4e^- + 4H_2O \longrightarrow 2H_2 + 4HO^- & (3) \\ 4h^+ + 4HO^- \longrightarrow 4HO\bullet & (4) \end{array} \right.$$

The resulting free HO• radical reacted with **1**. Fu et al. have postulated a mechanism that the h^+ oxidizes directly with the alcohol moiety of glucose (**1b**).[6] When the photocatalytic hydrogen evolution was performed using arabitol (**1c**) as a sacrificial reagent, the hydrogen evolutions were faster than in the case of **1a**. Moreover, the ratio of H_2 to CO_2 was constant at 2.5–3.0 even at low conversion, although the ratio of H_2 to CO_2 exceeded over 2.0 for stoichiometric values, due to the dissolution of CO_2 into the aqueous reaction solution. Judging

Table 1. The photocatalytic H_2 evolution from water using the saccharides **1** as a sacrificial reagent[a]

No	**1**/mg[b]		Catalyst /mg	Irradiation time/h[c]	Gas volume/mL			Molar ratio		N_{max}[e]	N[f]
					H_2	CO_2	Total[d]	H_2/**1**	H_2/CO_2		
1	**1a** ($C_5H_{10}O_5$)	150	75	12	94	47	173	4.2	2.0		
2	**1a**	150	100	12	111	34	208	5.0	3.3		
3	**1a**	150	125	12	97	30	182	4.4	3.3		
4	**1a**	150	150	12	85	26	165	3.8	3.3		
5	none	0	100	4	9	0	8	—	—		
6	**1a**	38	100	13	46	17	73	8.3	2.7		
7	**1a**	75	100	15	88	29	120	7.9	3.0		
8	**1a**	113	100	16	124	42	165	7.4	3.0		
9	**1a**	150	100	20	164	61	210	7.3	2.7	10	8.6
10	**1a**	188	100	30	187	76	234	6.7	2.5		
11	**1b** ($C_6H_{12}O_6$)	180	100	41	139	64	225	6.3	2.2	12	9.3
12	**1c** ($C_5H_{12}O_5$)	152	100	12	108	23	200	4.8	3.3	11	10.7
13	**1d** ($C_6H_{12}O_7$)	196	100	30	73	32	164	3.3	2.4	11	7.2
14	**1e** ($C_4H_7O_5^-$)	102	100	6	43	11	102	5.8	3.9	7	5.6
15	**1f** ($C_3H_8O_3$)	92	100	6	110	30	112	4.9	3.7	7	7.0
16	**1g** ($C_3H_6O_3$)	90	100	13	105	37	150	4.7	2.8	6	5.8
17	**1h** ($C_2H_4O_3$)	76	100	46	47	18	93	2.1	2.5	3	2.0
18	**1i** (CH_2O)[g]	30	100	13	44	18	84	1.8	2.5	2	1.9

[a] After the bubbling with N_2 gas to purge air, an aqueous solution (150 mL) containing varied amounts of **1** and Pt/TiO_2 (the content of Pt was 2 wt %) was irradiated. [b] Saccharides and the related compounds: xylose (**1a**), glucose (**1b**), arabitol (**1c**), gluconic acid (**1d**), calcium salt of L-theonate (**1e**), glycerol (**1f**), glycelaldehyde (**1g**), glycolic acid (**1h**), and methanal (**1i**). The amounts of **1** in mg. [c] Irradiation time to reach the maximum volume of hydrogen. In the cases of Runs 1–4, the irradiation for 12 h was fixed. [d] The gas volume in mL collected over water by a measuring cylinder. The collected gas was analyzed by GC. The collected gas involved H_2, CO_2, O_2, and N_2. [e] N_{max} is the maximum hydrogen amounts in mol evolved from the complete transformation of one mole of **1** which was calculated according to eq 5. [f] N is the limiting mole of hydrogen obtained from one mole of **1** obtained from the values of the intercept of the plots of H_2/**1a** against **1a**/catalyst. [g] Since 35% of the aqueous formaldehyde solution contained 7% methanol as a stabilizer, the hydrogen amounts were corrected by the subtraction of hydrogen from methanol.

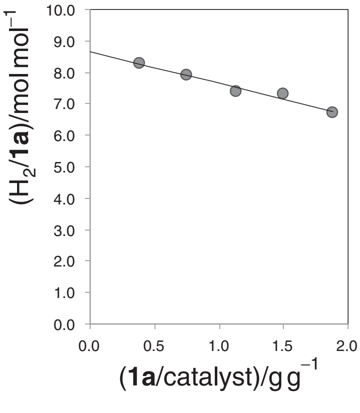
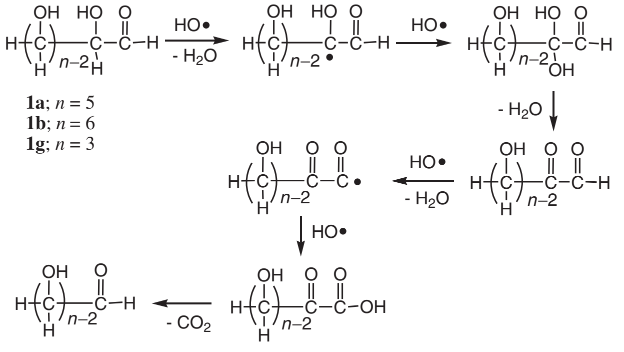


Figure 1. Dependence of H_2/**1a** on the **1a**/catalyst. Data from Runs 6–10 of Table 1. The N value was determined to be 8.6 from the intercept. Reaction conditions: [**1a**] = 38–188 mg, catalyst: 100 mg, water: 150 mL.



Scheme 2. A possible reaction scheme for the CO_2 evolution from saccharides **1** which were presented by Fisher form.

from these results, the free HO• radical underwent hydrogen abstraction from the α-carbon of alcoholic and formyl groups. It was suggested that the degradation of **1** proceeded by the sequential removal of CO_2 from the aldehyde group.[10] Therefore, we postulated Scheme 2 as one possible pathway. Formally the reaction of **1** with four equivalents of HO• radical eliminated one mole of CO_2 and three moles of H_2O from **1**. At the same time, 2 equivalents of H_2 evolved by the reduction of water with four electrons.

In order to examine the ability of saccharides as an electron source, photocatalytic hydrogen evolutions were performed for saccharides such as **1a**, **1b** ($C_6H_{12}O_6$), glycelaldehyde (**1g**, $C_3H_6O_3$), and methanal (**1i**, CH_2O) and the related compounds such as **1c**, gluconic acid (**1d**, $C_6H_{12}O_7$), calcium salt of L-theonate (**1e**, $C_4H_7O_5^-$), glycerol (**1f**),[11] and glycolic acid (**1h**, $C_2H_4O_3$).[12] The maximum hydrogen amounts in mol ($N_{max} = 0.5m + 2n - k$) evolved from the complete transformation of

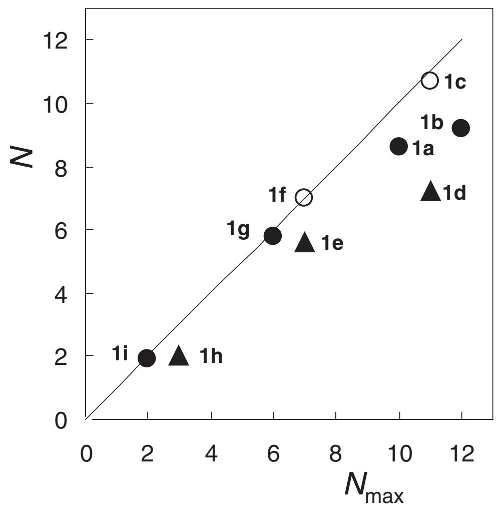
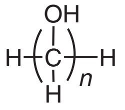


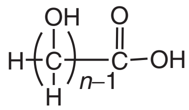
Figure 2. Plots of the N values vs. the N_{max} values of **1**: The aldehyde type (●), carboxylic type (▲), and alcohol type (○) of sacrificial reagents. The line is a line of $N = N_{max}$.

one mole of **1** ($C_nH_mO_k$) can be calculated according to eq 5 and are listed in Table 1.

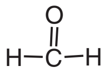
$$C_nH_mO_k + (2n - k)\ H_2O \longrightarrow nCO_2 + (0.5m + 2n - k)H_2 \quad (5)$$



1c; $n = 5$
1f; $n = 3$



1d; $n = 6$
1e; $n = 4$
1h; $n = 2$



1i

The N values of **1a**–**1i** were obtained from the intercept of the plots of $H_2/\mathbf{1}$ against $\mathbf{1}$/catalyst similar to Figure 1. Figure 2 shows the plots of the N values against the N_{max} values. In the cases of **1c**, **1f**, **1g**, and **1i**, the N values laid on a line of $N = N_{max}$, showing that stoichiometric H_2 evolution occurred, as has been reported for **1f**.[11] On the other hand, the N values of saccharides with $n \geq 4$ (**1a** and **1b**) and the carboxylic compounds (**1d**, **1e**, and **1h**) deviated from the line. In the decomposition procedure, **1a** and **1b** would be partially turned to materials not acting as sacrificial reagents. Thus, we found that one mole of pentose results in 8.6 equivalents of H_2 and 4.3 equivalents of CO_2, showing that pentose acted as a 17-electrons source to reduce the h^+ generated on TiO_2.

It has been established that the Pt/TiO_2-photocatalytic hydrogen evolution from water using a variety of sacrificial agents has been applied to reforming of alcohols[11,12] and decomposition of pollutants.[13–15] Here we can show the methodology to produce hydrogen from lignocellulosic biomass. We intend to obtain conversion from napiergrass to hydrogen by the combination of saccharification with cellulase and the hydrogen evolution with the Pt/TiO_2 catalyst.

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7 The Pt-doped TiO_2 was prepared as follow. An aqueous solution (50 mL) containing TiO_2 (1.0 g; ST-01, Ishihara Sangyo), $K_2[PtCl_6]$ (10–100 mg), and 2-propanol (0.38 mL) was irradiated by a high-pressure mercury lamp for 24 h under stirring. The optimized Pt content on TiO_2 was determined to be 2.0 wt % by the comparison of the amounts of hydrogen evolution by the Pt-doped TiO_2 (100 mg) under irradiation by a high-pressure mercury lamp for 6 h using glucose (100 mg) as sacrificial reagent.
8 Hydrogen, carbon dioxide, nitrogen, and oxygen were analyzed at temperature increasing from 40 to 180 °C on a Shimadzu GC-8A equipped with TCD detector using a stainless column (3 mmΦ, 6 m) packed with a SHINCARBON ST (Shimadzu).
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