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Sacrificial hydrogen production over TiO_2-based photocatalysts: Polyols, carboxylic acids, and saccharides

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ABSTRACT

Photocatalytic generation of H_2 from water over titanium dioxide (TiO_2) has received a great deal of interest for developing a renewable and clean energy source. It is initiated by charge-separation in TiO_2 upon photoexcitation. The electron reduces water to generate H_2 while the hole oxidizes hydroxide to generate hydroxyl radicals. However, water-splitting into O_2 and H_2 is not easy because of the large up-hill reaction and rapid reverse reaction. It is well known that the use of electron-donating sacrificial agents (hole scavengers) remarkably accelerates TiO_2-photocatalyzed H_2 evolution in which the hydroxyl radical is consumed by the sacrificial agents. Thus, sacrificial H_2 production over a TiO_2 photocatalyst is a convenient method to generate H_2 from biomass and waste. This paper reviews the sacrificial H_2 production from polyols, carboxylic acids, and saccharides, focusing on the chemical yield of H_2 production.

1. Introduction

The consumption of fossil resources causes serious environmental problems such as global warming and air pollution. As major issues in the current world, there is an urgent need to stop CO_2 levels increasing and to find new renewable energy sources to use instead of fossil fuels. Hydrogen production from water and solar energy (artificial photosynthesis) has received a great deal of attention while developing renewable and clean energy sources [1]. Titanium dioxide (TiO_2) has been a leading photocatalyst for the production of H_2 from H_2O since the discovery of photoelectrochemical H_2 evolution using TiO_2 by Honda and Fujishima [2]. Photocatalytic water-splitting over TiO_2 is initiated by charge-separation in TiO_2 upon photoexcitation [3]. The electron reduces water to generate H_2 while the hole oxidizes hydroxide to generate hydroxyl radicals [4]. In most cases, noble metals (Pt, Pd, and Au) are deposited onto the TiO_2 to accelerate the reduction of water by electrons, and electron-donating sacrificial agents (hole scavengers) are added to accelerate the consumption of hydroxyl radicals, thus enhancing H_2 evolution (sacrificial H_2 production) [5,6].

In general, TiO_2 can catalyze the three processes shown in Scheme 1. The photooxidation of organic compounds and pollutants with oxygen can easily proceed over TiO_2, since it is an extremely down-hill process (Scheme 1A). Water-splitting into O_2 and H_2 (Scheme 1B) is not an easy process because of the large up-hill reaction and rapid reverse reaction. Sacrificial H_2 production is an up-hill process but the energy change is small (Scheme 1C). Therefore, sacrificial H_2 production proceeds smoothly compared with water-splitting without sacrificial agents, thus providing a convenient method to generate H_2. The first study on sacrificial hydrogen production was reported by Kawai and Sakata in 1980 [7]. They succeeded in evolving H_2 from sugar and carboxylic acids in photocatalytic reactions over $RuO_2/Pt/TiO_2$ [7] and Pt/TiO_2 [8,9], respectively.

With this back ground, various kinds of reviews have been published. For example, water-splitting over TiO_2-based photocatalysts without sacrificial agents was reviewed by Ni et al. in 2007 [10]. Fornasiero et al. reviewed the photo-reforming of biomass-derived sacrificial agents over metal oxides in 2011 [11]. Moreover, Puga reviewed sacrificial photocatalytic H_2 production from biomass-derived materials from the viewpoint of the development of the photocatalyst in 2016 [12]. This paper reviews sacrificial H_2 production from polyols, carboxylic acids, and saccharides, focusing on the chemical yields of H_2 production.

2. Titanium oxide-based photocatalysts

The electrolysis of water proceeds theoretically by the application of

Abbreviations: PR, photo-reforming; SA, saccharification; SSF, simultaneous saccharification and fermentation; LMAA, low-moisture anhydrous ammonia pretreatment

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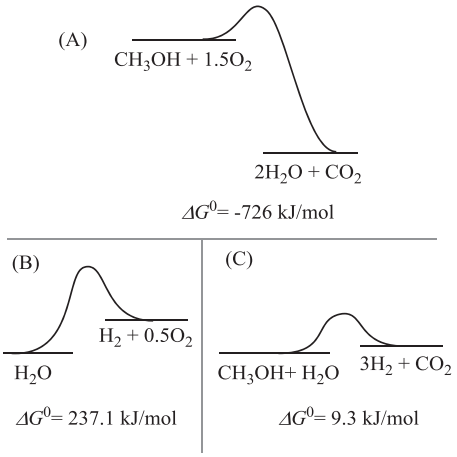

Scheme 1. Three types of energy diagrams for down-hill (A), large up-hill (B), and small up-hill processes (C).

1.23 V of voltage. Since water splitting is a two-electron process, 237.14 kJ mol^{-1} of energy is required [13]. TiO_2 can absorb a light at 384 nm which corresponds to 308.5 kJ mol^{-1} of excitation energy and exceeds the required energy. For photocatalytic reaction, almost all research has used TiO_2 in the form of P25 (Degussa Co. Ltd, Germany) and ST01 (Ishihara Sangyo Co. Ltd., Japan). P25 is prepared by hydrolysis of $TiCl_4$ and comprises 75% anatase and 25% rutile, whereas ST01 is prepared by hydrolysis of $TiOSO_4$ and comprises 100% anatase [14]. There are several methods to enlarge the surface area of TiO_2. For example, PEG (polyethylene glycol) was used as a pore-forming reagent to prepare porous TiO_2 [15]. Silica gel (SiO_2) supported TiO_2 was used to prepare a TiO_2-SiO_2 composite by mixing $Ti(OPr^i)_4$ with silica gel and then calcining [16].

In order to enhance the photocatalytic activity for H_2 evolution, a Pt-loaded TiO_2 (Pt/TiO_2) was used. A photo-deposition method developed by Kennedy III and Datye is the most popular method, which is performed by irradiating an aqueous slurry of TiO_2 in the presence of H_2PtCl_4 and ethanol [17]. Many researchers have used Pt/TiO_2 for sacrificial H_2 production [18–24]. Other noble metals such as Pd [25], Au [26,27], and Au-MO_x (M = Ag, Cu, Ni) [28] have been loaded onto TiO_2. Among the noble metal-loaded TiO_2 photocatalysts (1% Ag, 1% Au, 1% Pt, and 0.5% Pt), Pt/TiO_2 (Pt = 1 wt%) was the most active for H_2 production [29]. Other metals such as Cu [30], Ir, Ru, Rh, Ni [18], NiO [31,32], and RuO_2 [33] have also been loaded onto TiO_2. Kang et al. [34], Sun et al. [35], and Bandara et al. [36] succeeded in enhancing the reactivity of TiO_2 by the deposition of CuO instead of Pt. Fluorinated Pt/TiO_2 was prepared by flame spray pyrolysis of a precursor solution containing $Ti(OPr^i)_4$, propanoic acid, K_2PtCl_6 and C_6F_6 [37].

Table 1 summarizes the results of sacrificial hydrogen production over the TiO_2–based photocatalysts reported so far.

3. Alcoholic sacrificial agents (1)

Some typical alcoholic sacrificial agents are listed in Table 2. Early work on sacrificial H_2 production was performed in neat alcohols such as methanol (**1a**), ethanol (**1b**) and 2-propanol (**1d**) [38,39]. Now, most sacrificial H_2 production is performed in aqueous alcoholic solution. Aqueous solutions of **1a** are the most typical sacrificial agents used to evaluate and optimize photocatalytic activity. **1a** underwent oxidation up to CO_2 through the formation of formaldehyde and formic acid along with the formation of H_2 [19,40]. Kondarides et al. reported that the molar ratio of H_2 to CO_2 obtained from **1a** was experimentally confirmed to be 3:1 [41]. The decomposition mechanism of **1a** over Pt/TiO_2 was discussed on the basis of a direct interaction of **1a** with free or trapped holes in the TiO_2 [42], or via attack of the HO·radical

Table 1
Sacrificial H_2 production over TiO_2-based photocatalysts.

Sacrificial agent	Photocatalyst	Ref.
Sugar	RuO_2/Pt/TiO_2	[7]
CO	Pt/TiO_2	[69]
Ethanol (**1b**)	Pt/TiO_2	[45]
Glucose (**3e**)	Pt/TiO_2	[89]
CO	Pt/TiO_2	[68]
Carboxylic acid	Pt/TiO_2	[8]
Carboxylic acid	Pt/TiO_2	[9]
Methanol (**1a**), 2-Propanol (**1d**)	Ni/TiO_2 (Ni= 0.03–13.8 wt%)	[38]
1d	Pt/TiO_2	[50]
2-Propanol-d_8	TiO_2	[43]
1b, **1d**	M/TiO_2 (M = Pd, Pt)	[39]
Ascorbic acid (**3a**), Benzoic acid	Pt/TiO_2	[88]
1b	M/TiO_2 (M= Au, Pt)	[46]
1d, lysine	Pt/TiO_2	[64]
1b	Pt/TiO_2	[17]
1a	Pd/TiO_2	[25]
1a, **1b**	M/TiO_2 (M= Pt, Pd)	[42]
Oxalic acid (**2b**)	Pt/TiO_2 (Pt= 0.5 wt%)	[81]
1a	Pd/TiO_2	[22]
Formic acid (**2a**), **2b**	Pt/TiO_2	[82]
1a	Pd/TiO_2	[23]
1a	Pt/TiO_2	[6]
1a	Cu/TiO_2 (Cu= 1.2 wt%)	[30]
1a	CuO/TiO_2 (CuO= 7 wt%)	[36]
1a	RuO_2/TiO_2	[33]
Alcohols	M/TiO_2 (M = Pd, Pt, Rh)	[70]
$ClCH_2CO_2H$, Cl_2CHCO_2H	Pt/TiO_2	[86]
1a	Pt/TiO_2	[20]
1b	Pt/TiO_2	[48]
1a, **1b**, CH_3CO_2H (**2d**)	Pt/TiO_2 (Pt= 0.5 wt%)	[41]
1a	M/TiO_2 (M = Pd, Pt, Au)	[18]
1a	Cu/TiO_2	[34]
Glycerol (**1h**)	Pt/TiO_2 (Pt= 0.5 wt%)	[54]
1h	M/TiO_2 (M= Pd, Pt, Au)	[79]
1a	Pt/TiO_2 (Pt= 1.0 wt%)	[21]
1a	Au/TiO_2	[27]
2a	$SrTiO_3$	[83]
1a, **1b**, **1d**	Pt/TiO_2	[15]
1a	Au/TiO_2	[26]
1h	Pt-N-TiO_2	[55]
2d	Pt/TiO_2 (Pt= 1.0 wt%)	[87]
Glycolic acid (**2c**)	TiO_2 under O_2	[84]
1h, **3e**, Sucrose (**3j**)	Heteroatom (N, B)-doped Pt/TiO_2	[61]
1a	CuO/TiO_2	[35]
1h	M/TiO_2 (M = 0.5 wt% Pd, 2.0 wt% Au)	[59]
1a	Thin film TiO_2[a]	[119]
1a	M/TiO_2 (M= Ag, Au, Pt)	[29]
Carbohydrates	Pt/TiO_2	[90]
3e	Pt/TiO_2 (Pt= 0.10 wt%)	[91]
1a	M/TiO_2 (M= 0.5 wt%Pt, 1.0 wt% Au)	[44]
1d	Pt/TiO_2 (Pt= 1.0 wt%)	[49]
1h	Pt/TiO_2	[57]
1h	CuO/TiO_2	[60]
1h	Pt/TiO_2 (Pt= 1.0 wt%)	[76]
C4, C3- polyols	Pd/TiO_2 (Pd= 0.3 wt%)	[77]
2d	TiO_2	[85]
Lactic acid (**2e**)	CdS/Pt/TiO_2[a]	[115]
1a	Pt/TiO_2	[40]
Methylamine, Dimethylamine	TiO_2	[66]
1h, **3e**, **3j**	M/TiO_2 (M = Pd, Pt, Au)	[92]
1h	Pt/TiO_2	[62]
Ammonia	Pt/TiO_2	[99]
Ammonia, Methylamine	Pt/TiO_2	[65]
Xylose	Pt/TiO_2	[93]
1b	Pt/TiO_2 (Pt= 0.06–1.0 wt%)	[47]
1h	Pt/TiO_2	[56]
1h	Pt/TiO_2 (Pt= 0.1–0.5 wt%)	[59]
3e	M/TiO_2 (1 wt% of M= Pd, Au)	[80]
Polyols	Pt/TiO_2 (Pt= 1.0 wt%)	[51]
Monools	Pd/TiO_2	[75]
1b	SiC-TiO_2[a]	[117]
1b	SiO_2-Pt/TiO_2[a]	[16]
1a	Cu/S-TiO_2[a]	[116]

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