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Photocatalytic Hydrogenation on Semiconductor Particles

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1. Introduction

Photocatalytic hydrogenation on semiconductor particles is a quite unique methodology compared to the conventional hydrogenations such as catalytic hydrogenation on metals or homogeneous catalysis using metal complexes. The catalysis can be defined as a light-driven redox reaction at a solid/liquid or a solid/gas interface. The semiconductor photocatalysis have been mainly developed by researchers in the areas of photochemistry, electrochemistry, and heterogeneous catalysis. Since Fujishima and Honda have discovered the photoelectrochemical water splitting upon titanium dioxide (TiO_2) photoelectrode in the early 1970's [1], the heterogeneous photocatalysis, especially using TiO_2 , has been applied to various fields such as storage of solar energy [2,3], environmental purification [3,4], and specific surface properties of self-cleaning, self-sterilizing, and anti-fogging induced by incident light [5]. The photocatalysis has also attracted much attention with respect to inducing characteristic organic transformations since 1970's [6-11]. Among those, the photocatalytic hydrogenation of ethene and ethyne on TiO_2 was already reported in 1975 [12]. Since then, the reductive photocatalysis has been applied to the hydrogenation for several organic compounds having various double or triple bonds.

Herein, we summarize the progress in photocatalytic hydrogenations covering the literatures available up to 2011. At first, we introduce the fundamentals of semiconductor photocatalysis in order to understand the mechanistic principles. Next, we review the reports on applications to the photocatalytic hydrogenation. Here, we refer to scope and limitation of the photocatalytic hydrogenation on semiconductor particles. Advantages and disadvantages using this method are also compared to those of the conventional hydrogenations. Finally, prospects of the photocatalytic hydrogenation are discussed.

2. Fundamentals

Some metal oxides (e.g. titanium dioxide (TiO_2) etc.) and sulfides (e.g. cadmium sulfide (CdS), zinc sulfide (ZnS) etc.) are regarded as semiconductors, in which electrons (e^-) photogenerated in conduction band (CB) and holes (h^+) simultaneously generated in valence band (VB) play important roles in electroconductivity as well as chemical reactivities on the surface, i.e. e^- and h^+ can induce redox reactions as shown in Fig. 1. This reaction system is so called “a micro-photoelectrochemical cell”, consisting of an anode and a cathode within a small particle. The hydrogenation generally proceeds as the reduction of an electron acceptor (**A**) followed by the protonation as depicted in Fig. 1. The photocatalytic reduction of **A** can be carried out in the presence of a large excess amount of electron donor (**D**) such as alcohols or amines, and in the absence of molecular oxygen (O_2). The aim using the electron donor (**D**) is to scavenge hole generated in VB, thereby diminishing the degree of recombination between e^- and h^+ within the semiconductor particles. Thus, it is important for the reductive hydrogenation of organic substrates to choose an appropriate electron donor (**D**) as hole scavenger. Moreover, it is necessary to purge O_2 gas from the reaction system in order to improve the reduction efficiency, since O_2 acts as a competitive electron acceptor.

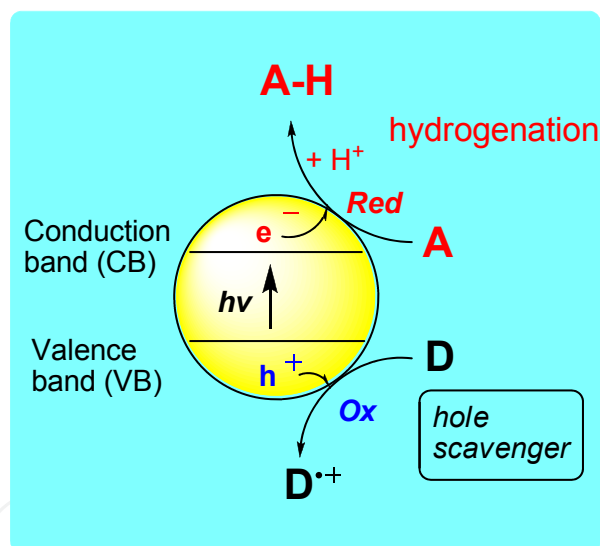


Figure 1. Mechanistic principle of photocatalytic hydrogenation on a semiconductor particle

Important points in the semiconductor photocatalyst materials are band gap energy between CB and VB and potential energy levels of CB and VB. The band gap energy defines the minimum photon energy absorbed by the semiconductor materials: Band gap (eV) = $1240/\text{wavelength (nm)}$. Therefore, if a photocatalyst possesses less than 3.1 eV band gap, it can absorb photons with visible light region ($> 400 \text{ nm}$). Fig. 2 indicates the band gaps and the band levels (V vs. standard hydrogen electrode (SHE) at pH 7) of TiO_2 (anatase), TiO_2 (rutile), ZnS , and CdS semiconductor materials as measured photoelectrochemically [8]. TiO_2 has four polymorphs: rutile (tetragonal, the most stable phase), anatase (tetragonal), brookite (orthorhombic), and TiO_2 (B) (monoclinic), in which rutile and anatase have been

mainly used as photocatalysts. The band gap of anatase (3.2 eV) is slightly larger than that of rutile (3.0 eV), because the CB level of anatase is located at 0.2 eV more negative than that of rutile as depicted in Fig. 2. In order to proceed the photocatalytic reaction effectively, the bottom level of CB has to be more negative than a reduction potential of **A** ($A/A^{\cdot-}$), while the top level of VB has to be more positive than an oxidation potential of **D** (D^+/D) as shown in Fig. 2.

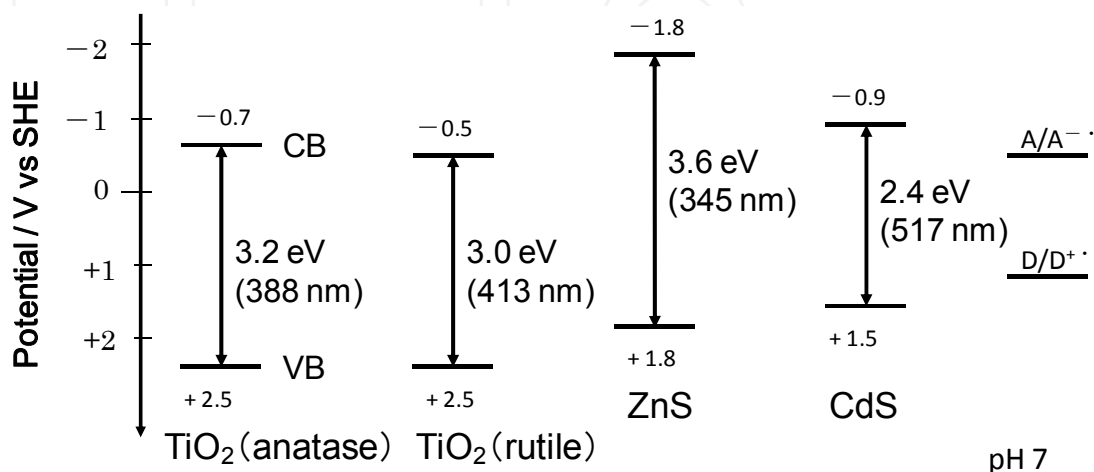


Figure 2. Band gaps and band edge positions of some semiconductor photocatalysts

It should be also noted that the band levels usually shift with a change in pH (-0.059 V/pH) for oxide materials. In addition to this pH dependence, surface impurities, adsorbed compounds, and the change to organic solvents would induce band shifts. For an example, the negative band shift is observed when water is replaced by organic solvents such as acetonitrile and alcohols [13]. The negative CB level is essential for the photoreductive hydrogenation reaction. From this point of view, ZnS and CdS having the negative CB level are effective candidates for the photocatalytic hydrogenation. However, these sulfides can be oxidized by h^+ in the absence of an appropriate hole scavenger: CdS or $ZnS + 2h^+ \rightarrow Cd^{2+}$ or $Zn^{2+} + S$, which is so called “photocorrosion” [8]. Thus, the choice of a suitable hole scavenger (solvent) is particularly important for hydrogenation using ZnS or CdS.

It is important to estimate a quantum yield (QY) in photocatalytic reactions. QY is defined as the number of events which occurs per photon absorbed by a photocatalyst as follows:

$$QY = \frac{(\text{number of reacted electrons or holes})}{(\text{number of absorbed photons})}$$

However, it is difficult to determine the real number of photons absorbed by a photocatalyst in a dispersed system because of light scattering by the photocatalyst powder. Therefore, in general, an apparent QY as described below is applied to the actual photocatalytic reactions.

$$\text{Apparent } QY = \frac{(\text{number of reacted electrons or holes})}{(\text{number of incident photons})}$$

The apparent QY is estimated to be smaller than the real QY because the number of absorbed photons is usually smaller than that of incident photons.

Loading of fine particles, usually nanometer size of noble metals (e.g. platinum (Pt) or silver (Ag) etc.) or metal oxide (nickel oxide (NiO) etc.), on the photocatalyst surface often improves the reaction efficiency as a co-catalyst due to the following reasons: (1) the particles enhance the charge separation between e^- and h^+ and prevent the charge recombination, and (2) the particles act as effective reactive sites in the photocatalytic transformation processes. For an example, Pt fine particles loaded on photocatalyst greatly improve the chemical efficiency of hydrogen evolution from water or alcohol under irradiation.

3. Applications

3.1. Hydrogenation of alkenes and alkynes

Photocatalytic hydrogenation of ethene and ethyne firstly reported by Boonstra and Mutsaers in 1975 [12]. Some hydrogenated products have been found upon the UV illumination (320 – 390 nm) of TiO_2 in an atmosphere of ethene or ethyne. Main products from ethene were methane, ethane, propane, and *n*-butane, whereas, in the case of ethyne, the products were methane, ethene, ethane, and propane. In these reactions, the hydrogen source has been thought to be the surface Ti-OH group on TiO_2 .

Anpo and co-workers investigated the photocatalytic hydrogenation of various alkenes and alkynes in the presence of water vapor upon TiO_2 [14-17]. Major products on the UV illuminated TiO_2 powders were the compounds formed by hydrogenation accompanied by C=C or C≡C bond fission [14, 15]. In contrast, a significant enhancement of hydrogenation products without the bond fission has been observed on the UV illuminated Pt-loaded TiO_2 (Pt/ TiO_2) powders [16]. Especially, the Pt-loaded rutile TiO_2 predominantly catalyzed the hydrogenation of propyne ($CH_3C\equiv CH$) to afford C_3H_6 and C_3H_8 (C_3/C_2 ratio = 5.60) as listed in Table 1. Anpo et al. further investigated the size effects on Pt/ TiO_2 particles in the photocatalytic hydrogenation of $CH_3C\equiv CH$ with H_2O [17]. Quantum yields of the whole photoreactions became smaller with increasing the particle size of Pt/ TiO_2 (rutile), whereas selectivity of the hydrogenation products without vs. with the bond fission (C_3H_8/C_2H_6) reversely became larger and reached at $C_3H_8/C_2H_6 = 99$ upon the particle size of 200 nm.

Catalysts Type	Products (10^{-9} mol m^{-2} h^{-1})					C_3/C_2 ratio
	CH_4	C_2H_6	C_2H_4	C_3H_6	C_3H_8	
TiO_2 (P25 ^a)	1.90	12.3	0.40	1.10	0.50	0.12
Pt ^b / TiO_2 (P25 ^a)	2.40	15.7	0.50	15.7	0.40	0.86
TiO_2 (rutile)	0.55	3.27	0.10	0.48	0.19	0.17
Pt ^b / TiO_2 (rutile)	0.22	1.60	0.23	10.3	1.10	5.60

^a A composition ratio of rutile/anatase is ca. 1/4. ^b 4wt%

Table 1. The amount of products formed in the photocatalytic hydrogenation of $CH_3C\equiv CH$ on the four type of TiO_2 in the presence of water vapor at 300 K [16].

The hydrogenation of C-C multiple bonds of alkenes and alkynes was also examined in alcohols using Pt/TiO₂ powders by Yamataka et al. [18]. In this case, some saturated alkanes were produced in good yields (> 50% after 24 h), while the alcoholic solvents were concurrently oxidized to the corresponding carbonyl compounds. Baba et al. have synthesized bimetal-loaded TiO₂ such as Pd/TiO₂/Ni or Pt/TiO₂/Cu and applied those to the hydrogenation of ethene [19]. The hydrogenation to ethane was efficiently occurred upon the bimetal/TiO₂, on which the role of the latter metals (Ni or Cu) was to suppress the hydrogen production as side reaction. Titanium-silicon (Ti/Si) binary oxides were prepared and utilized for the photocatalytic hydrogenation of alkenes and alkynes with H₂O by Anpo's group [20-22]. The reactivity and selectivity for the hydrogenation of CH₃C≡CH were investigated as a function of the Ti content [21, 22]. It was found that the hydrogenation with bond fission producing C₂H₆ and CH₄ was predominant in regions of low Ti content, whereas the hydrogenation yielding C₃H₆ proceeded in regions of high Ti content. They have revealed that tetrahedrally coordinated titanium oxide species played a significant role in the efficient photoreaction with a high selectivity for the hydrogenation with the bond fission, while the catalysts involving the aggregated and octahedrally coordinated titanium dioxide species showed a high selectivity for the hydrogenation producing C₃H₆, being similar to reaction using the powdered TiO₂ catalysts. Molybdenum oxide or sulfide complexes supported on TiO₂ were developed by Kunts and applied to the photocatalytic hydrogenation of ethyne [23, 24]. The sulfur systems were somewhat more efficient in the hydrogenation, and also favored the 2 electron-transferred product ethene rather than the 4 electron-transferred product ethane.

Yanagida et al. reported that visible light response CdS nanocrystallites (2 – 5 nm) catalyzed the efficient hydrogenation of electron-deficient alkenes with triethylamine (TEA) (Table 2) [25]. This reaction is the first example of visible light induced hydrogenation of alkenes on semiconductor particles. The hydrogenation (two electron reduction) was always accompanied with *cis-trans* isomerization (one electron reduction /oxidation process). The yield of the hydrogenation becomes favorable with increasing light intensity [26]. TEA was used for a sacrificial electron donor, in which the oxidation reaction proceeded as follows: Et₃N + H₂O + 2h⁺ → Et₂NH + CH₃CHO + 2H⁺.

$\begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \text{R}^1 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R}^2 \end{array} + 2\text{H}^+ + 2\text{e}^-$		$\xrightarrow[\text{TEA in MeOH}]{\text{CdS, } > 400 \text{ nm}}$		$\begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
R ¹	R ²	Time / h	Conversion / %	Yield / %	-E _{red} ^a / V
CO ₂ CH ₃	CO ₂ CH ₃ (<i>cis</i>)	2	100	70	1.56
CO ₂ CH ₃	CO ₂ CH ₃ (<i>trans</i>)	2	100	60	1.60
<i>p</i> -CNC ₆ H ₄	CN (<i>cis</i>)	3	70	47	1.75
<i>p</i> -CNC ₆ H ₄	CN (<i>trans</i>)	3	68	41	1.73
<i>p</i> -CNC ₆ H ₄	CO ₂ CH ₃ (<i>cis</i>)	3	100	76	1.75
<i>p</i> -CNC ₆ H ₄	CO ₂ CH ₃ (<i>trans</i>)	3	100	92	1.75
C ₆ H ₅	CO ₂ CH ₃ (<i>trans</i>)	3	10	trace	1.98

^a Polarographic half-wave reduction potential vs. SCE in MeOH.

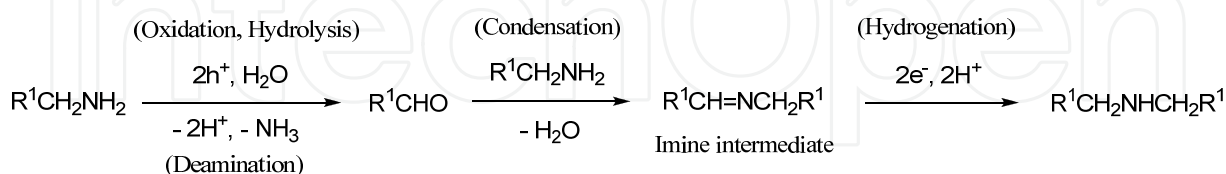
Table 2. CdS-catalyzed photohydrogenation of alkenes with triethylamine in MeOH [25].

3.2. Hydrogenation of imine, azo, and azide compounds

Hydrogenation of the C=N bond of imine intermediates upon the Pt/TiO₂ and CdS photocatalysts was observed during some inter- or intramolecular deaminocondensations in one-pot reaction systems as reported by Ohtani and co-workers [27, 28]. Fig. 3 illustrates the photocatalytic transformation of primary amine to symmetrical or asymmetrical secondary amines via the photocatalytic deaminocondensation in water or alcohols. In water [27], a primary amine was firstly oxidized by two holes to form an imine (R¹CH=NH) followed by hydrolysis to give a corresponding aldehyde (R¹CHO). Next, the aldehyde was condensed with another amine to yield the imine intermediate (R¹CH=NCH₂R¹). Finally, the imine was photocatalytically hydrogenated to produce the symmetrical secondary amine (R¹CH₂NHCH₂R¹). On the other hand, in alcoholic solvent [28], the alcohol molecule (sacrificial hole scavenger) was primarily oxidized by two holes to afford the corresponding carbonyl compound (R²R³C=O) which was also condensed with amine to yield the imine intermediate (R²R³C=NCH₂R¹). The imine was further hydrogenated to form the asymmetrical secondary amine (R²R³CHNHCH₂R¹). This mechanistic principle has been used for several inter- or intramolecular reaction systems as depicted in Scheme 1. Furthermore, photocatalytic deaminocyclization of L-lysine to pipecolic acid was examined using TiO₂ and CdS, and concluded that these two photocatalysts exhibited the different stereochemistry [29, 30].

Kisch et al. found that photocatalytic hydrogenation of azobenzene to hydrazobenzene on ZnS or CdS proceeded as a side reaction of a photocatalyzed addition of 3,4-dihydropyran to azobenzene giving 1-(3,4-Dihydro-2H-pyran-4-yl)-1,2-diphenylhydrazine (DPDH) (Scheme 2) [8, 31]. The formation of the hydrazobenzene was strongly favored when Pt-loaded ZnS or Pt-loaded CdS was used as the photocatalyst. This would be caused by the two electron-transfer process preferentially occurred on the platinum fine particles.

(A) in water



(B) in alcohol

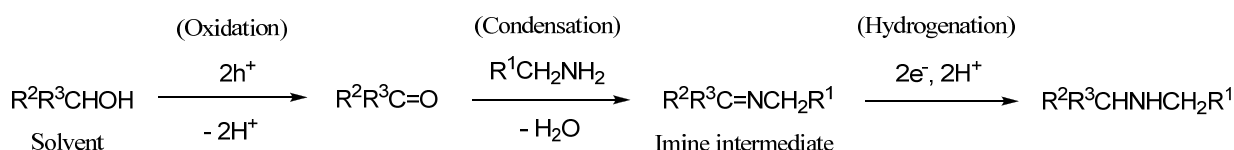
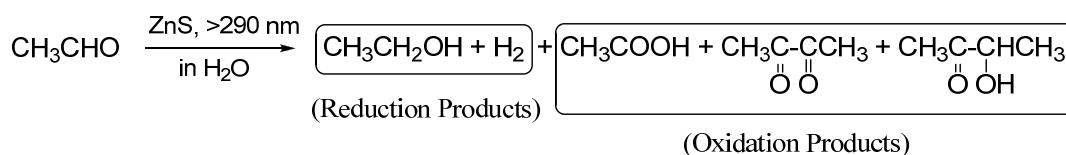


Figure 3. Deaminocondensation reactions in one pot system containing hydrogenation process.

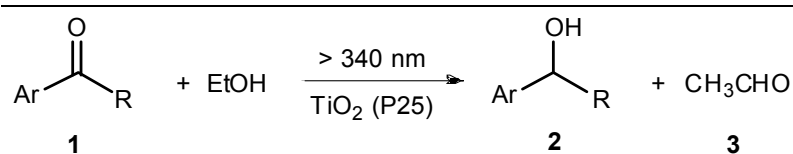
in ethanol as summarized in Table 3 [37]. Acetaldehyde was simultaneously produced in the oxidation of ethanol by h^+ generated in the VB or those trapped at the surface sites on TiO_2 . The desired secondary alcohols were obtained in almost quantitative yields for more than ten examples: e.g. acetophenone ($\text{Ar} = \text{C}_6\text{H}_5$, $\text{R} = \text{Me}$) to 1-phenylethanol in 97% yield (highlighted in gray color in Table 3). They also found that most of the reaction rates depend on the reduction potential (E_{red}) of substrates, except for 2,2,2-trifluoroacetophenone [37]. In general, aldehydes are more reactive than ketones because of electronic and steric factors. Electrochemically, E_{red} of aldehydes are more positive than those of ketones. However, the hydrogenations of aldehydes were accompanied with competitive formation of by-products such as diethyl acetal etc., leading to erosion of chemical efficiency.

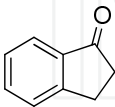
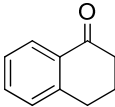
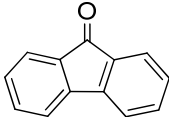
Aliphatic aldehydes and ketones were hydrogenated by using the ZnS photocatalyst, because the CB level of ZnS is sufficiently negative as indicated in Fig. 2 [38, 39]. In contrast, the photocatalytic hydrogenation did not occur upon TiO_2 , since the CB level of TiO_2 is too positive to reduce the aliphatic ketones [37]. Yanagida and co-workers reported that acetaldehyde was reduced and oxidized upon the UV irradiated ZnS nano-crystallites (2 – 5 nm) in water as depicted in Scheme 3 [38]. The reduction products were ethanol and H_2 generated by the photocatalytic reduction of H_2O , while acetaldehyde was oxidized by the photogenerated holes to produce acetic acid, diacetyl, and acetoin. The apparent quantum yield of ethanol (main product) formation was 0.25 at 313 nm. The similar result was observed in the photocatalytic reaction of propionaldehyde on the ZnS nano-crystallite [38]. The ZnS nano-crystallites were further applied to the photocatalytic hydrogenation of aliphatic ketones such as acetone, 2-butanone, 3-pentanone, 2-hexanone, cyclopentanone, and cyclohexanone in the presence of sacrificial hole scavengers of S^{2-} and SO_3^{2-} (Oxidation reaction: $\text{S}^{2-} + \text{SO}_3^{2-} + 2h^+ \rightarrow \text{S}_2\text{O}_3^{2-}$) [39]. Most of examined ketones were photocatalytically hydrogenated at comparable rates to give the alcohols in almost quantitative yields except for acetone. The apparent quantum yield for the formation of 2-butanol was 0.27 at 313 nm.

Yanagida et al. applied the visible light response CdS nanocrystallite to the photoreduction of aromatic ketones [25, 26, 40]. Two types of the reduction products, secondary alcohols from two electron-transfer process and pinacols from one electron-transfer process, were observed as listed in Table 4, while the oxidation of TEA as a sacrificial electron donor by the VB holes afforded diethylamine and acetaldehyde. The yields of the hydrogenation involving two electron-transfer process were preferable for substrates possessing the electron-withdrawing group ($-\text{CN}$ or $-\text{Cl}$) as shown in Table 4, and further became favorable with increasing light intensity [26] and with decreasing the particle size [40].



Scheme 3. Photocatalytic reduction and oxidation reactions of acetaldehyde in water on ZnS.



Substrates (1)		Time (h)	Conversion (%)	Yield of 2 (%)	Yield of 3 (%)	$-E_{\text{red}}$ (V) ^b
Ar	R					
C ₆ H ₅	H	1	100	76±2	57	1.99
C ₆ H ₅	Me	4	100	97±2	>99	2.13
C ₆ H ₅	Et	8	91	87	>99	2.18
C ₆ H ₅	<i>i</i> -Pr	8	24	25	32	2.21
C ₆ H ₅	<i>t</i> -Bu	8	17	7	42	2.24
C ₆ H ₅	CF ₃	8	70	63	10	1.59
C ₆ H ₅	C ₆ H ₅	4	82	78	97	1.83
2-MeC ₆ H ₄	Me	8	66	63	84	2.16
4-MeC ₆ H ₄	Me	8	100	>99	>99	2.15
2-FC ₆ H ₄	Me	3	100	99	>99	1.86
3-FC ₆ H ₄	Me	3	100	97	>99	2.04
4-FC ₆ H ₄	Me	4	100	>99	>99	2.15
2,6-F ₂ C ₆ H ₄	Me	5	100	96	94	-
C ₆ F ₅	Me	2	100	>99	>99	1.83
1-C ₁₀ H ₇	H	1	95	76±3	77	1.66
1-C ₁₀ H ₇	Me	10	100	>99	93	1.86
2-C ₁₀ H ₇	H	1	94	32±7	93	1.70
2-C ₁₀ H ₇	Me	5	100	94±4	>99	1.73
		8	100	>99	>99	2.06
		8	100	91	>99	-
		2	82	81	98	1.42

^a Carried out for a mixture of the substrate **1** (3 mmol) and the P25 TiO₂ (0.1 g) in deaerated EtOH (30 cm³) under UV irradiation (>340 nm) at 32 °C. ^b Reduction potential vs. SCE in CH₃CN containing Bu₄NClO₄ electrolyte.

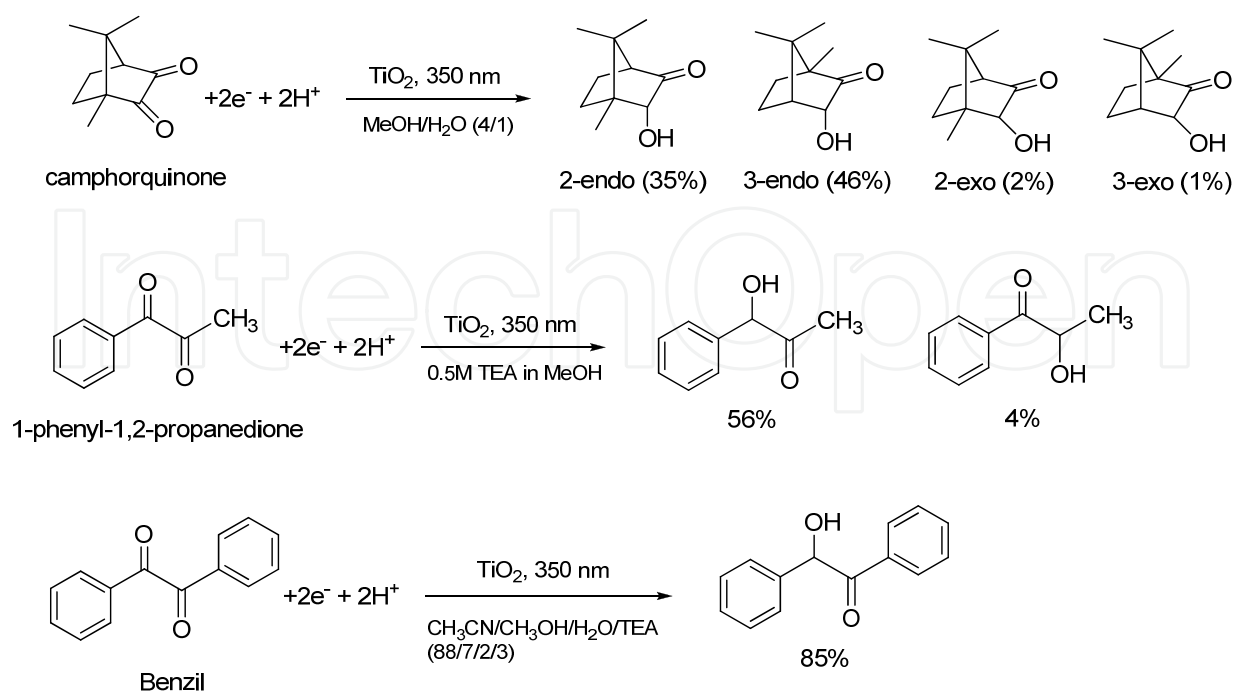
Table 3. Photocatalytic hydrogenation of aromatic carbonyl compounds on P25 TiO₂ [37].^a

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array} + 2\text{e}^- + 2\text{H}^+ \xrightarrow[\text{Et}_3\text{N in MeOH}]{\text{CdS, } >400 \text{ nm}} \begin{array}{c} \text{H} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R}^1 \quad \text{R}^2 \end{array} \quad \text{and/or} \quad \begin{array}{c} \text{R}^2 \quad \text{R}^2 \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{R}^1 \quad \text{OH} \quad \text{OH} \end{array} $						
4			5		6	
Substrates (4)		Time	Conversion of	Yield of	Yield of	$-E_{\text{red}} \text{ (V)}^a$
R ¹	R ²	(h)	4 (%)	5 (%)	6 (%)	
<i>p</i> -CNC ₆ H ₄	C ₆ H ₅	2	100	95	0	1.17
<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	3	98	70	12	1.32
<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	3	98	90	4	1.35
C ₆ H ₅	C ₆ H ₅	3	100	95	5	1.55
<i>p</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	3	97	33	56	1.56
<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	3	52	15	40	1.56
C ₆ H ₅	CH ₃	3	10	trace	80	2.00

^a Polarographic half-wave reduction potential vs. SCE in MeOH.

Table 4. Photocatalytic hydrogenation of aromatic ketones on nanocrystallized CdS [25].

1,2-Diketones such as camphorquinone, 1-phenyl-1,2-propanedione, and benzil were hydrogenated to the corresponding α -hydroxyketones in moderate to good yields on the UV-irradiated P25 TiO₂ as shown in Scheme 4 [41, 42]. The yields and stereoselectivities were increased in the presence of water or TEA as a sacrificial electron donor in methanol solvent. The endo-hydroxycamphors were formed much more favorably than the exo-products, though there was little selectivity between 2 and 3 positions.



Scheme 4. Photocatalytic hydrogenations of diketone compounds upon the P25 TiO₂ powder.

3.4. Hydrogenation of carbon dioxide

With increasing concerns about rising atmospheric CO₂ concentration, the need for research to utilize CO₂ in chemical synthesis has been increased greatly [43]. Therefore, the photocatalytic hydrogenation of CO₂ upon semiconductor powders has received much attention [9-11, 44-56]. Among the earliest studies on the photocatalytic hydrogenation of CO₂, Inoue et al. examined a wide range of semiconductors (WO₃, TiO₂, ZnO, CdS, GaP, and SiC in 200 – 400 mesh) in aqueous solution [44]. The results indicated that CO₂ was reduced to HCOOH, HCHO, and CH₃OH, and the product yields correlated to the position of the CB level of the semiconductors. In the case of WO₃, since the CB level was insufficiently negative to reduce CO₂, no reduction products were observed. In contrast, SiC having the most negative CB level gave the highest yields. Later, Henglein and Gutiérrez reported that high quantum yield of 0.20 was achieved in the hydrogenation of CO₂ to formate using ZnS colloidal suspension under UV light irradiation [45]. Here, the solvent was a mixture of water and ethanol, or 2-propanol as the hole scavenger. After the earliest works, a great deal of effort has been devoted to studying the photocatalytic reduction of CO₂. Most of works are summarized in recent reviews [9-11], in which the use of TiO₂, SrTiO₃, ZrO, ZnS, or CdS is reported. Recently, visible-light-driven new materials were developed and applied to the photocatalytic reduction of CO₂ under visible light irradiation: for examples, InTaO₄ [46], LaCoO₃ [47], BiVO₄ [48], ZnGaO₄ [49], Zn₂GeO₄ [50, 51], Bi₂WO₆ [52] etc.

The photocatalytic reduction of CO₂ on semiconductor powders gives several reduction products such as CO, HCOOH, HCHO, CH₃OH, CH₄, and various hydrocarbons. Among those, methanol is the most valuable product because it can be directly used as a fuel or a building block. High efficiency and selectivity in the preparation of methanol were obtained by the use of Ti-oxide/Y-zeolite catalysts containing highly dispersed tetrahedral titanium oxide species under UV irradiation [53, 54]. The charge-transfer excited state of these species played an important role in the selectivity for producing CH₃OH, in contrast to the different selectivity giving CH₄ on bulk TiO₂ photocatalyst. Ti-incorporated mesoporous silica also exhibited high activity in the photoreduction of CO₂ with water to generate CH₃OH and CH₄ under UV irradiation [55]. Methanol was also selectively produced by employing CaFe₂O₄ [56] and NiO-loaded InTaO₄ [47] under visible light irradiation.

3.5. Hydrogenation of Nitrate and nitrite ions, and nitroaromatics

The use of artificial fertilizers in agriculture has caused a great deal of concern regarding water pollution induced by production of nitrate (NO₃⁻) and nitrite (NO₂⁻) ions from the fertilizers [57]. Therefore, chemical processes for elimination or hydrogenation of NO₃⁻ ions have been extensively studied photocatalytically. TiO₂ photocatalyst has been used for the hydrogenation of NO₃⁻ and NO₂⁻ ions to ammonia [58-60]. Other photocatalysts such as SrTiO₃ [61], K₄NbO₁₇ [61], tantalate oxides (K₃Ta₃Si₂O₁₃, BaTa₂O₆, KTaO₃, NaTaO₃) [62], and ZnS [63], have also been reported as active photocatalysts for the hydrogenation of nitrate ions under UV light irradiation. It is worth noting that Kudo et al. developed a 0.1% nickel doped ZnS (Zn_{0.999}Ni_{0.001}S) photocatalyst to extend the photocatalytic response of ZnS

toward visible region [64], and applied it into the reduction of NO_3^- and NO_2^- ions under visible light irradiation [65]. The amounts of products and electrons consumed in the reduction of NO_3^- and NO_2^- are listed in Table 5. The ratios of the amounts of $\text{NH}_3/\text{NO}_2^-$ and NH_3/N_2 increased in the presence of the platinum cocatalyst, indicating that selectivity for the NH_3 production was improved by the Pt loading on $\text{Zn}_{0.999}\text{Ni}_{0.001}\text{S}$. More recently, Yamauchi and co-workers reported highly selective ammonia synthesis from nitrate with photocatalytically generated hydrogen on CuPd nanoalloys loaded on TiO_2 , on which ammonia was selectively produced up to 78% yield with hydrogen evolution under UV light irradiation [66].

Catalysts Type	Reactant (initial conc./ molL^{-1})	Amounts of products (electron consumed)/ μmol			
		H_2^b	NO_2^-	NH_3	N_2
non-loaded	no NO_3^- nor NO_2^- (0)	214 (428)	(-)	(-)	(-)
non-loaded	NO_3^- (1.0)	60 (120)	250 (500) ^c	21 (168) ^d	2.7 (27) ^e
1wt% Pt-loaded	NO_3^- (1.0)	212 (424)	14 (28) ^c	11 (88) ^d	0.79 (7.9) ^e
non-loaded	NO_2^- (0.01)	37 (74)	(-)	41 (246) ^f	2.4 (14) ^g
1wt% Pt-loaded	NO_2^- (0.01)	96 (192)	(-)	65 (390) ^f	9.5 (57) ^g

^a Carried out for a mixture of reactant (NO_3^- or NO_2^-) and photocatalyst powder (0.5 g) in aqueous CH_3OH solution (6.25 vol%) under visible light irradiation ($>420\text{ nm}$) for 20 h.

^b A by-product from the reduction of water: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$.

^c $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$. ^d $\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$. ^e $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$. ^f $\text{NO}_2^- + 7\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_3 + 2\text{H}_2\text{O}$. ^g $2\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$.

Table 5. Reduction of NO_3^- and NO_2^- on $\text{Zn}_{0.999}\text{Ni}_{0.001}\text{S}$ photocatalysts [65].^a

Several organic nitroaromatics can be easily hydrogenated to afford corresponding amino compounds in the presence of sacrificial hole scavenger upon the UV irradiated TiO_2 as firstly reported by Li and co-workers in 1993 [67]. Since then, the photocatalytic hydrogenation of nitro compounds using some kinds of semiconductor photocatalysts was extensively studied by a number of researchers. The hydrogenation reactions proceeded almost quantitatively. The details are summarized in recent reviews [9-11]. Recent progress in this research has been directed toward the development of visible light response photocatalysts such as nitrogen-doped TiO_2 [68] and dye-sensitized TiO_2 loaded with transition metal nanoparticles [69].

4. Advantages and disadvantages using this method

Compared to the conventional hydrogenation methods as mentioned in other Chapters, the photocatalytic hydrogenation on semiconductor particles has some great advantages: (1) The most important merit is that particular reducing agents (e.g. H_2 gas etc.) are not necessary in this method. In most case, the reductants are conventional solvents such as water, alcohols, and amines which concurrently act as hole scavengers. Therefore, this method allows us to avoid both the use of harmful and dangerous chemical reagents and the emission of harmful waste. (2) The reactions mostly proceed under mild conditions, e.g.

under ordinary temperature and pressure, and therefore are safety. (3) In the case of TiO_2 or other stable metal oxide photocatalysts, the materials are chemically stable, easily removal, and reusable. These three significant advantages imply that this method holds great promise to become an alternative “green” synthetic method.

On the other hand, a disadvantage of this method is to be unsuitable for a large-scale synthesis, because the rate of surface reaction on photocatalysts under irradiation are limited by electron-hole recombination, smaller surface area, lesser adsorptive and diffusive properties of substrates compared to those of the conventional catalysis. Therefore, up to now, scaling-up of the semiconductor photocatalysis has been successfully applied only to wastewater treatment, in which solar photocatalytic degradation of water contaminants, persistent toxic compounds and cyanide etc., is carried out on low concentration of the contaminants [70, 71]. In contrast, highly chemoselective and stereoselective hydrogenations have been made on a pilot plant scale and even fewer are available commercially on a multi kg scale by the conventional heterogeneous or homogeneous hydrogenation methods [72].

5. Concluding remarks and future directions

The photocatalytic hydrogenation on semiconductor particles has developed as the highly efficient and selective reaction during the past three decades. For examples, the selective hydrogenations were reported for the reactions of $\text{CH}_3\text{C}\equiv\text{CH}$ to $\text{CH}_3\text{CH}=\text{CH}_2$ on Pt/TiO_2 (rutile) [17], the aromatic ketones to the corresponding secondary alcohols on the P25 TiO_2 [37], the aliphatic ketones to the corresponding alcohols on the ZnS nano-crystallite [39], and nitroaromatics to the corresponding amino-compounds on TiO_2 [67-69]. In addition, the selective formation of methanol from CO_2 [53-56] and NH_3 from NO_3^- [65, 66] has been received much attention to solve the environmental issues. Recent progress in the reductive hydrogenation has been directed toward the development of visible light response photocatalysts to utilize solar energy effectively [46-52, 65, 68, 69].

One of the most significant features of semiconductor photocatalysis is that we can utilize both oxidation and reduction in one-pot processes as mentioned in the deaminocondensation reactions [27-30]. The combination of redox reactions can afford several unique reactions, which are not achieved by conventional reaction techniques. Thus, the semiconductor photocatalysis is one of promising methods in fine chemical synthesis for high value pharmaceuticals etc. In order to achieve this method, development of highly stereoselective photocatalysis will be indispensable, although less known about such semiconductor photocatalysts so far. Therefore, particular attention should be directed toward the development of new enantioselective semiconductor catalyzed reactions in the future.

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