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Dehydrogenation of Primary Aliphatic Alcohols by Au/TiO₂ Photocatalysts

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Dehydrogenation reaction of primary aliphatic alcohols to aldehydes and molecular hydrogen was achieved under UV–vis light irradiation in the presence of gold-loaded titanium dioxide (Au/TiO₂) photocatalysts.

Keywords: Dehydrogenation | Aldehyde | Photocatalysis

Acceptorless dehydrogenation of primary alcohols (RCH₂OH) to aldehydes (RCHO) and molecular hydrogen (H₂) is an important reaction in synthetic chemistry. Emerging alternatives to conventional thermal methods include photocatalytic dehydrogenation using (metal-loaded) inorganic photocatalysts such as Pt/TiO₂,⁴ Pt/CdS,⁵ CdS,⁶ Ru/SrTiO₃:Rh,⁷ Pd/CdS–TiO₂,⁸ Au–Pd/ZrO₂,⁹ and Ni/CdS¹⁰; the photocatalytic dehydrogenation proceeds at around room temperature (25–50 °C) under ultraviolet (UV) or visible (vis) light irradiation, producing aldehydes in a chemoselective manner.⁴⁻¹⁰ Although these methods are effective for converting benzyl and allyl alcohols, selective dehydrogenation of simple aliphatic primary alcohols to aldehydes remains elusive due to the lower reactivity of unactivated alcohols and the instability of aliphatic aldehydes under the reaction conditions.^{11,12} For example, our visiblelight-promoted dehydrogenation of 1-decanol with a Ru/SrTiO₃:Rh photocatalyst gives 1-decanal in 51% yield (25 °C, 24 h), but is accompanied with over-oxidation to 1decanoic acid (15%).⁷ A Au–Pd/ZrO₂ photocatalyst developed by Zhu and coworkers promotes selective conversion of 3phenylpropanol to 3-phenylpropanal under visible light irradiation but the reaction proceeds in low yield (31% yield, 45 °C, 16 h).9 Here, we report selective dehydrogenation of primary aliphatic alcohols to aliphatic aldehydes and H₂ under UV-vis light irradiation using gold-loaded titanium dioxide (Au/TiO₂) photocatalysts.

We first prepared several metal-loaded titanium dioxide photocatalysts (M/TiO₂, M = Pd, Pt, Ag, or Au) by means of an impregnation-reduction method using Aeroxide TiO₂ P25 (Evonik) and sodium borohydride (Table S1),¹³ and we tested their photocatalytic activity for dehydrogenation of 3phenylpropanol (1a, 2.0 mmol) in ethyl acetate at 45 °C for 1 h under UV-vis irradiation (300 W Xe lamp with a UV cold mirror, $\lambda = 300-470$ nm) under a nitrogen atmosphere (Table 1). The palladium, platinum and gold-loaded photocatalysts showed high reactivity and selectivity for this transformation, generating 3-phenylpropanal (2a) in 11-14% GC yield with nearly equimolar amounts of H₂ (12-16% GC yield, Table 1, Entries 1, 2, and 4). Ag/TiO₂ was less effective than the other three photocatalysts (Entry 3).^{13b} The metal loading amount of the most reactive photocatalyst, Au/TiO₂,^{14,15} could be reduced to 0.6 wt % without affecting the reactivity and

Table 1. Photocatalytic dehydrogenation of 3-phenylpropanol (1a) to 3-phenylpropanal (2a) and H_2 .^{*a*}

Û	∼∕OH 1a	$hv(\lambda = 30)$ M/TiO ₂ ethyl acet	00–470 r ate, N ₂		2a	°O _{+ H2}
Entry	М	Т	t	Conv.	Yield	Yield
	(loading in wt %)	(°C)	(h)	of 1a (%) ^b	of 2a (%) ^b	of H ₂ (%) ^b
1	Pd (5)	45	1	10 ± 2	11 ± 1	13 ± 1
2	Pt (5)	45	1	14 ± 2	12 ± 1	12 ± 1
3	Ag (4)	45	1	4^c	3 ^{<i>c</i>}	2^{c}
4	Au (5)	45	1	17 ± 2	14 ± 1	16 ± 2
5	Au (0.6)	45	1	17 ± 1	17 ± 1	17 ± 3
6	None	45	1	2^d	1^d	$< 1^{d}$
7^e	Au (0.6)	45	1	$< 1^d$	$< 1^{d}$	$< 1^{d}$
8	Au (0.6)	25	1	9 ± 1	9 ± 1	4 ± 2
9	Au (0.6)	65	1	23 ± 2	20 ± 1	18 ± 1
10	Au (0.6)	45	10	69 ± 7	55 ± 9	$N.D.^{f}$
11	Au (0.6) ^g	45	10	98 ± 1	51 ± 4	$N.D.^{f}$
12 ^{<i>h</i>}	Au (0.6) ^g	45	10	87 ± 7	76 ± 5	$N.D.^{f}$

^aConditions: **1a** (2.0 mmol, 269.7 \pm 1.2 mg), UV–vis light (300 W Xe lamp with a UV cold mirror, $\lambda = 300-470$ nm), M/TiO₂ (39 mg), ethyl acetate (5 mL), N₂. ^bDetermined by GC analysis, average of 3 runs with standard deviation. ^cAverage of 2 runs. ^dResult of a single run. ^eWithout light irradiation. ^fNot determined due to evolution of larger amounts of hydrogen. ^gAu/TiO₂ loading: 117 mg. ^hEthyl acetate (25 mL).

selectivity (Entry 5). The reaction rate of 340 μ mol h⁻¹ in this case was higher than in previously reported examples [4.3 μ mol h⁻¹ (Ru/SrTiO₃:Rh)⁷; 19 μ mol h⁻¹ (Au–Pd/ZrO₂)⁹; 0.3 µmol h⁻¹ (Ni/CdS)¹⁰], and the Au loading-based turnover frequency (TOF) was 310 h⁻¹. Dehydrogenation hardly proceeded in the absence of photocatalyst (Entry 6) or without light irradiation (Entry 7). Decreasing the temperature from 45 °C to 25 °C significantly reduced the reaction rate (Entry 8), and the reactivity at 65 °C was slightly higher than that at 45 °C (reaction rate: 400 µmol h⁻¹, Au loading-based TOF: 360 h^{-1} , Entry 9). Conversion of **1a** reached 69% and 98% when the reaction mixture was irradiated for 10 h in the presence of 39 mg and 117 mg of Au/TiO₂, respectively (Entries 10 and 11). Lower selectivity in these cases could be overcome by diluting the reaction mixture, and the aldehyde 2a was obtained in 76% GC yield (Entry 12).¹⁶

The scope of the photocatalytic dehydrogenation of primary aliphatic alcohols is illustrated in Table 2. Straightchain fatty alcohols could be effectively converted to aldehydes **2b** and **2c** in good yield, whereas β - or γ -branched primary alcohols **1d–1f** were less reactive under these conditions, though the aldehydes were formed under the reaction conditions in moderate yields. Major side products in these experiments were alkanes (R–H). Carboxylic acids Table 2. Photocatalytic dehydrogenation of alcohols.^a

R^ОН 1	$hv(\lambda = 300)$ Au (0.6 wt ° ethyl aceta 45 °C, 10 h	$ \begin{array}{c} -470 \text{ nm} \\ \frac{8}{7} \\ \frac{7}{100_2} \\ \text{te, N}_2 \\ \end{array} \\ R \\ \end{array} \\ R \\ C \\ R \\ C \\ \end{array} + $	H ₂
$RCH_2OH\left(1\right)$	Conv. $(\%)^b$	RCHO (2)	Yield $(\%)^{b,c}$
ОН	98		85 (66)
1a		2a	
<i>n</i> -C ₁₂ H ₂₅ OH (1b)	94	<i>n</i> -C ₁₁ H ₂₃ CHO (2b)	82 (74)
<i>n</i> -C ₁₈ H ₃₇ OH (1c)	89	<i>n</i> -C ₁₇ H ₃₅ CHO (2c)	70 (59)
ОН	> 99	Δ	69 (64)
1d		2d	
M ₆ OH	68	$M_6 = 0$ M_4	54^d (45)
1e		2e	
ОН	78	A-o	46 ^{<i>d</i>}
1f		2f	
CI OH	97	CI M7 O	71 (55)
	98 98	^{2g}	83 (63)
1h		2h	

^{*a*}Conditions: **1** (2.0 mmol), UV–vis light (300 W Xe lamp with a UV cold mirror, $\lambda = 300-470$ nm), Au (0.6 wt %)/TiO₂ (117 mg), ethyl acetate (25 mL). ^{*b*}Determined by ¹H NMR analysis, average of 2 runs. ^cIsolated yield of **2** in parentheses, result of a single run. ^{*d*}Result of a single run.

Table 3.	Compatibility	of functional	groups."
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1a + impurity $\frac{hv, \text{Au/TiO}_2}{\text{ethyl acetate}}$ 2a + recovered N ₂ , 45 °C, 10 h						
Entry	Impurity	Yield of $2a (\%)^b$	Recovery impurity $(\%)^{b}$	of		
1	None	76 ± 5	-			
2	Cyclohexanone	77	> 98			
3	Chlorobenzene	79	> 98			
4	Benzonitrile	57	> 98			
5	Nitrobenzene	23	89			

^{*a*}Conditions: **1a** (2.0 mmol), impurity (2.0 mmol), UV–vis light (300 W Xe lamp with a UV cold mirror, $\lambda = 300-470$ nm), Au (0.6 wt %)/TiO₂ (117 mg), ethyl acetate (25 mL). ^{*b*}Determined by GC analysis.

(RCO₂H) and esters (RCO₂CH₂R) were not observed. Reactions with allyl alcohols (*e.g.* cinnamyl alcohol), benzyl alcohols (*e.g.* 3-methoxybenzyl alcohol), or secondary alcohols (*e.g.* 2-tetradecanol) were sluggish, and the desired aldehydes or ketones were detected in low yields (< 40%). The presence of the C_{sp3}–Cl bond in **1g** or the C=C bond in **1h** was well tolerated under the photocatalytic conditions, and the functionalized aldehydes **2g** and **2h** were obtained in good yields.

Functional group compatibility was further examined by adding impurities to the reaction mixture (Table 3). Functional groups such as cyclic ketone, C_{Ar} -Cl bond, and cyano group did not react under the photocatalytic conditions (Entries 2–4). Compared with the data in Table 3, Entry 1, the efficiency of dehydrogenation of **1a** remained essentially

unchanged in the presence of ketone or aryl chloride (Entries 2 and 3), but the presence of nitrile slightly retarded dehydrogenation of **1a** (Entry 4). More reactive nitrobenzene markedly inhibited dehydrogenation of **1a** with partial conversion of the impurity, yet **2a** was still formed in 23% yield (Entry 5).



Figure 1. Molar compositions of (a) 1a, (b) 2a, and (c) ethylbenzene in photocatalytic dehydrogenation of 1a with Au (0.6 wt %)/TiO₂. The reaction mixture was left in the dark during 2–4 and 6–8 h. See Table 1, Entry 12 for reaction conditions and Table S4 for detailed results.

photocatalytic То better characterize this dehydrogenation reaction, we conducted a series of experiments using cutoff filters ($\lambda > 350$, 370, and 400 nm). The results indicated that this reaction is mainly promoted by UV light irradiation ($\lambda = 350-470$ nm, yield of **2a**: 64%; 370-470 nm, 51%; 400-470 nm, 2% Table S3). This finding is broadly in line with the band gap of TiO₂ (Figure S1).^{14,17} The Au/TiO₂-promoted quantum yield for apparent dehydrogenation of alcohols using UV light (365 nm monochromatic light) was 20% (average of 2 runs), which was higher than we had previously with Ru/SrTiO₃:Rh (0.9%, 420 nm monochromatic light).⁷ The high apparent quantum yield for Au/TiO2-promoted dehydrogenation of alcohols under UV-light irradiation would be a main reason for the higher TOF of this reaction. Monitoring of Au/TiO2-promoted dehydrogenation of 1a with or without UV-vis light irradiation indicated that both consumption of 1a and formation of 2a occurred only when the reaction mixture was irradiated (Figure 1). The composition of 1a and 2a remained unchanged when the reaction mixture was left in the dark (2-4 h and 6-8 h), indicating that formation of 2a is due to lightpromoted dehydrogenation of 1a. Although small amounts of ethylbenzene was detected in the late stage of reaction (< 10%), the dehydrogenation continuously gave 2a with good selectivity. The Au/TiO2 photocatalyst was found to be recyclable at least for four consecutive dehydrogenation of 1a by separating the photocatalyst after each run and reactivating it with NaBH₄ (Table S5). The activity of the recycled Au/TiO₂ remained essentially unchanged in these four runs [TOF = 74, 88, 71, and 84 h^{-1} (t = 2 h)].

In summary, selective dehydrogenation of primary aliphatic alcohols to aldehydes was effectively promoted by Au/TiO_2 photocatalysts under mild conditions. This photocatalytic system provides a platform for in situ generation of aliphatic aldehyde and hydrogen, both of which play key roles in so-called borrowing hydrogen chemistry.^{1,13}

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