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Titania-Photocatalyzed Transfer Hydrogenation Reactions with Methanol as a Hydrogen Source: Enhanced Catalytic Performance by Pd–Pt Alloy at Ambient Temperature

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Hydrogenation reactions are of great importance in scientific research and in industry productions. Herein, we designed a novel system to realize photocatalytic transfer hydrogenation by using solar light as the energy input and methanol as the hydrogen source. In this reaction, titania loaded with Pd–Pt bimetallic alloy nanocrystals as a cocatalyst exhibited photocatalytic performance that was remarkably superior to that exhibited by titania with Pd or Pt alone as the cocatalyst. This work has shed light on the rational design of multifunctional catalysts through selecting appropriate bimetallic alloys as efficient cocatalysts.

The selective hydrogenation of organic functional groups is of great significance for the industrial production of fine chemicals, pharmaceutical intermediates, and many other products.[1,2] Traditional heterogeneous hydrogenation reactions always employ high temperatures and pressurized molecular hydrogen, which clearly cause mass energy consumption and explosion hazards in operation. A mild heterogeneous hydrogenation process is highly favorable from the perspective of academic research and practical applications.[3,4] Titania photocatalysis, owing to its mild reaction conditions and the sustainability of the energy source (solar light) employed, has attracted intensive research interest and has been widely applied in the elimination of environmental pollutants, in organic synthesis, and in hydrogen evolution.[5–10] Among various applications, titania-photocatalyzed organic synthesis routes are especially appealing because of novel reaction mechanisms. Various types of these reactions have been realized through photocatalysis, such as oxidation, reduction, isomerization, and polymerization.[11–15]

However, as a result of the low reduction potential of the electrons in the photoinduced conduction band [−0.5 V vs. normal hydrogen electrode (NHE)] and the strong oxidizing power of the valence band holes (+2.7 V vs. NHE), titania-photocatalyzed reduction reactions are not as popular as oxidation reactions.[5,12,16] To realize efficient photocatalytic reduction reactions, it is crucial to enhance the reducing power of the catalyst. It has been found that loading of noble metals as cocatalysts on titania can significantly improve the reducibility of the titania photocatalyst.[17,18] By choosing appropriate noble metals as cocatalysts, some unsaturated organic functional groups are expected to be effectively reduced under light illumination. In addition, photocatalytic reductions are always accompanied by oxidation reactions.[19] Methanol, which may be derived from biomass, can play a dual role and act as both the sacrificial agent and the effective hydrogen donor. This route, if realized, will possess desirable advantages, such as the use of a green and sustainable energy source, mild reaction conditions, and a transfer hydrogenation mechanism.

As to the noble metal cocatalyst, platinum (Pt) has been widely applied in titania-photocatalyzed water splitting for its high activity towards the reduction of protons to produce hydrogen, whereas palladium (Pd) is an efficient catalyst in hydrogenation reactions with the use of molecular hydrogen under high temperatures.[17] By combining titania with the Pt and Pd cocatalysts, photocatalytic transfer hydrogenation reactions could be realized under mild reaction conditions. Moreover, as a result of the different work functions of Pt and Pd, electron migration can happen between closely contacted Pt and Pd clusters, which thereby leads to the formation of relatively positively charged Pt sites (electron deficient) and negatively charged Pd sites (electron redundant) on the surface of the Pd–Pt alloy particles.[20–22] Such heterogeneity of the surface electron distribution can positively contribute to enhanced catalytic activity.[23,24] Therefore, the Pd–Pt alloy is apparently a suitable cocatalyst for titania to realize photocatalytic transfer hydrogenation reactions efficiently.

Herein, for the first time, we report studies on photocatalytic transfer hydrogenation reactions catalyzed by titania with a Pd–Pt alloy cocatalyst. A series of organic chemicals with different types of unsaturated functional groups were selectively reduced with hydrogen derived from methanol under mild reaction conditions, that is, light irradiation and ambient temperature. In these reactions, the cocatalyst, titania loaded with the Pd–Pt alloy in a weight ratio of 7:3, exhibited remarkably enhanced photocatalytic performance relative to that exhibited by pure Pd- or Pt-loaded titania. The hydrogen-transfer reac-

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tion mechanism was also confirmed by hydrogen isotope tracer studies.

The titania used in this work was P25, which is commercially available and composed of an anatase–rutile mixed phase. The photocatalyst (Pd–Pt/TiO_2) was prepared by the photoreduction method (see the Experimental Section for details). The amount of alloy loaded was 1.2 wt%, and the photocatalysts with different Pd/Pt weight ratios are denoted by Pd_xPt_{100-x}/TiO_2, such as $Pd_{70}Pt_{30}/TiO_2$, which indicates that the titania was loaded with 1.2 wt% of the alloy with a Pd/Pt weight ratio of 7:3.

The average titania crystal size was 25.7 nm [calculated from the anatase (1 0 1) diffraction peak by using the Scherren equation], and the BET surface area of titania was 44.8 m^2g^{-1} (Figure S1, Supporting Information). As shown in Figure 1 b, the lattice distance of 0.35 nm corresponds to the anatase (1 0 1) and (0 1 1) planes with a dihedral angle of 82°. Rutile crystals with (1 1 0) lattice spacing of 0.33 nm are also clearly observed. Because Pd and Pt share the same facet-centered cubic (fcc) structure and because their lattice constant is almost identical with only 0.77% mismatch, they can easily form bimetallic nanocrystal alloys if their ions exist in the reducing environment.[25] In the high-resolution TEM images of Pd/TiO_2, $Pd_{70}Pt_{30}/TiO_2$, and Pt/TiO_2, the Pd, Pd–Pt alloy, and Pt particles on titania are all approximately the same in size, that is, 5 nm. Figure S2 show the X-ray photoelectron spectroscopy (XPS) patterns of the photocatalysts. The peaks located at binding energies of 334.8 and 70.8 eV correspond to Pd $3d_{5/2}$ and Pt $5f_{7/2}$, respectively.

As shown in the UV/Vis spectra (Figure 2), the absorbance of Pd/TiO_2 and Pt/TiO_2 in the UV region is lower than that of pure titania. However, with the bimetallic alloy as the cocatalyst, the absorbance of $Pd_{70}Pt_{30}/TiO_2$ in the UV region increased dramatically relative to that of pure Pt- or Pd-loaded titania and pure titania. These changes in absorbance result from the formation of the alloy structure.[23,26] Moreover, the enhanced UV absorbance of the sample, in photocatalysis, is of great significance for improved photocatalytic performance.[27]

Reduction of acetophenone was chosen as the model reaction to test the feasibility of the photocatalytic transfer hydrogenation reaction [Eq. (1)]. With methanol as the hydrogen donor, acetophenone was selectively reduced to 1-phenylethanol on Pd/TiO_2 upon irradiation at room temperature (Figure 3, Table S1). As the percentage of Pt in the Pd–Pt alloy was increased, the photocatalytic activity of Pd–Pt/TiO_2 increased dramatically, and the optimum performance was obtained on $Pd_{70}Pt_{30}/TiO_2$ with a conversion of 94.3% and a selectivity for 1-phenylethanol of 92.3% within 2.5 h of light irradiation. Further increases in the percentage of Pt in the alloy resulted in decreased catalytic activity of the photocatalysts. On Pt/TiO_2, the transfer hydrogenation reaction proceeded with a very low yield of the product. The above investigations clearly confirmed the feasibility of the photocatalytic transfer hydrogenation reaction and the enhancement resulting from the alloy cocatalyst in this process.

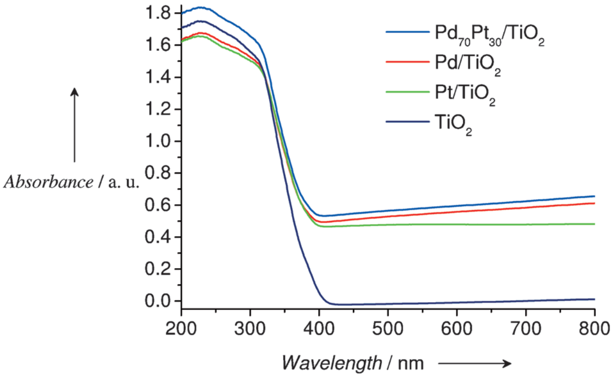


Figure 2. Diffuse reflectance UV/Vis spectra of the photocatalysts.

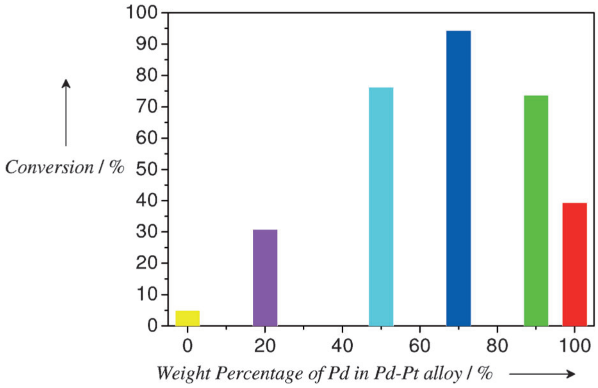
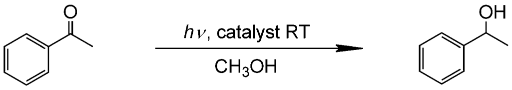


Figure 3. Catalytic performance of Pd_xPt_{100-x}/TiO_2 with different Pd–Pt weight ratios in the transfer hydrogenation of acetophenone.



(1)

To further confirm the universality of this photocatalytic transfer hydrogenation reaction with methanol as the hydrogen source and the beneficial effect of the alloy, Pd/TiO_2, $Pd_{70}Pt_{30}/TiO_2$, and Pt/TiO_2 were used in the reduction of a series of substrates with unsaturated carbonyl and alkene functional groups. As shown in Table 1,

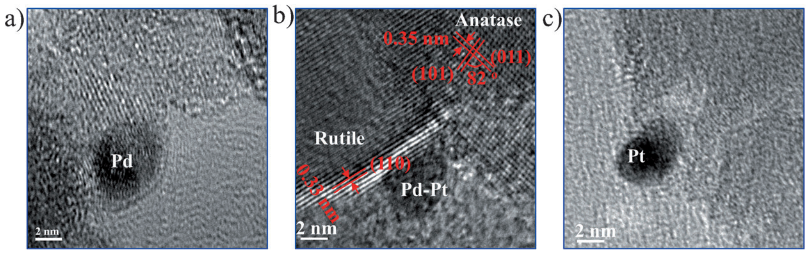
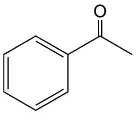
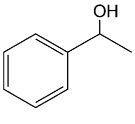
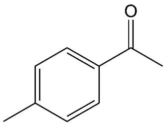
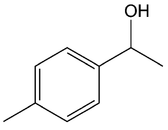
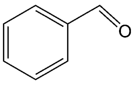
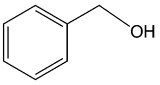
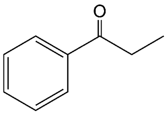
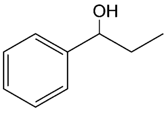
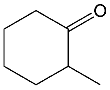
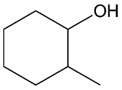
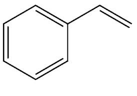
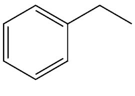
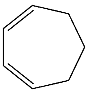
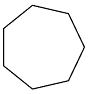
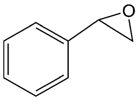
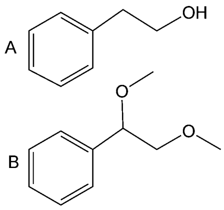
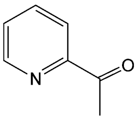
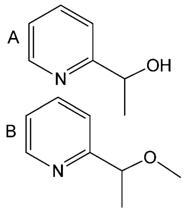


Figure 1. High-resolution TEM images of the photocatalysts: a) Pd/TiO_2, b) $Pd_{70}Pt_{30}/TiO_2$, and c) Pt/TiO_2.

Table 1. Photocatalytic transfer hydrogenation reactions of a series of organic substrates on the photocatalysts.[a]

Entry	Reaction time [h]	Substrate	Product	Conversion [mol %] (Selectivity [%])		
				Pd/TiO_2	$Pd_{70}Pt_{30}/TiO_2$	Pt/TiO_2
1	2.5			39.3 (97.9)	94.3 (92.3)	5.0 (31.1)
2	6.5			12.1 (99.1)	63.6 (92.3)	5.2 (51.3)
3	2			40.5 (81.8)	98.3 (90.6)	46.1 (99.0)
4	1.5			23.8 (96.5)	99.8 (99.0)	4.2 (16.9)
5	6			6.9 (99.0)	63.0 (99.0)	0 (–)
6	2			17.2 (88.5)	99.7 (95.2)	7.7 (88.5)
7	2.25			69.1 (96.0)	99.8 (96.2)	6.3 (88.9)
8	4			95.9 (A: 15.0, B: 63.6)	99.8 (A: 30.9, B: 54.2)	87.2 (A: 11.6, B: 77.7)
9	4.5			72.9 (A: 68.9, B: 11.6)	95.6 (A: 89.0, B: 5.4)	71.8 (A: 51.1, B: 19.4)

[a] Reaction conditions: The reaction mixture was prepared by adding photocatalyst (9 mg), substrate (0.1 mmol) and toluene (0.1 mmol, internal standard) in methanol (5 mL). The mixture, in a 10 mL Pyrex glass vial, was deoxygenated through argon bubbling. The mixture was magnetically stirred and irradiated with a 300 W xenon lamp (PE300BF).

several aromatic ketones were hydrogenated to produce the corresponding aromatic alcohols with high selectivity (Table 1, entries 1–4). The methyl-substituted aromatic ketone (Table 1, entry 2) was less reactive, but a longer reaction time led to a higher conversion without severely decreasing the selectivity of the product. In terms of aliphatic ketones (Table 1, entry 5), 2-methylcyclohexanone was reduced to 2-methylcyclohexanol with a high selectivity of 99% on Pd/TiO_2 and $Pd_{70}Pt_{30}/TiO_2$. Although Pt-loaded titania was not active in this hydrogenation reaction, with the addition of Pt in Pd, the conversion on $Pd_{70}Pt_{30}/TiO_2$ increased almost 10-fold relative to the conversion on Pd/TiO_2. This transfer hydrogenation reduction reaction was also applied to some alkenes, such as styrene and 1,3-cycloheptadiene (Table 1, entries 6 and 7). As to styrene oxide, selectivity to the direct 2-phenylethanol hydrogenation product was low, and the main product resulted from condensation reactions of the reduction intermediates with methanol (Table 1, entry 8). An acetyl group connected to a heteroaromatic ring was also selectively reduced to a hydroxy group with the formation of minor condensation byproducts (Table 1, entry 9). Most importantly, in all of the transfer hydrogenation reactions, $Pd_{70}Pt_{30}/TiO_2$ clearly exhibited photocatalytic performance that was superior to that of pure Pt- or Pd-loaded titania, which firmly validates the enhanced effect of the alloy cocatalyst in the transfer hydrogenation reaction. This enhancement effect may result from the synergistic effect of the Pt and Pd sites in the production of the active hydrogen species and in the addition of hydrogen to the substrate, respectively. In addition, the aforementioned surface electron heterogeneity and the improved UV absorbance also contribute to the enhanced photocatalytic activity of titania loaded with a Pd–Pt bimetallic alloy cocatalyst.

With hydrogen isotope tracing studies, we were able to understand the reaction mechanism of this photocatalytic hydrogenation reaction more clearly. Reduction of acetophenone was employed as a model reaction. With CH_3OH as the hydrogen donor, the mass spectrum of 1-phenylethanol presents a molecular ion peak at $m/z = 122$ $[M^+]$. With CH_3OD as the hydrogen donor, the molecular ion peaks shift to $[M^+ + 1]$ and

[M^++2]. The [M^++1] peak corresponds to 1-phenylethanol, which results from the reduction of the carbonyl group of acetophenone by the addition of one deuterium atom and one hydrogen atom; the [M^++2] peak is the product obtained after hydrogenation of acetophenone by two deuterium atoms (Figure S3).

According to all of the above investigations, we tentatively proposed a reaction mechanism for the photocatalytic transfer hydrogenation reaction (Figure 4). Upon irradiation, photoinduced conduction band electrons (e^-) and valence band holes (h^+) are generated in the titania crystals. The photoinduced electrons are transferred to the noble metal cocatalyst, owing to the lower Fermi energy level of Pt and Pd relative to the conduction band of titania.[17,28] The valence band holes with strong oxidizing power diffuse to the surface of the titania particles to initiate the oxidation of the adsorbed methanol into formaldehyde or other deep-oxidation products, and this is accompanied by the release of hydrogen ions. The photoinduced electrons on the surface of the noble metal reduce the protons into hydrogen atoms, which results in the formation of surface hydride species that are ready to react with the unsaturated C=O or C=C groups of the surface-adsorbed substrate molecules. The energy of the photons ($h\nu$) powers the catalytic cycle, which constantly transfers hydrogen from methanol to the target substrate.

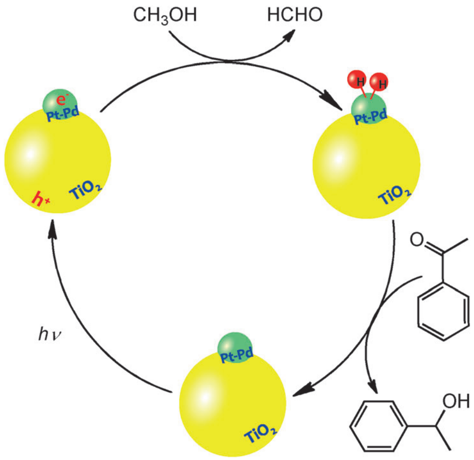


Figure 4. Proposed reaction mechanism for the photocatalytic transfer hydrogenation reduction of acetophenone.

In conclusion, heterogeneous photocatalytic transfer reductions were realized on Pd–Pt/TiO_2 with methanol as the hydrogen donor; this initiated a novel strategy of combining light energy and methanol (possibly from biomass) to realize a significant hydrogenation process under mild reaction conditions. Moreover, TiO_2 loaded with Pd–Pt alloy nanocrystals at a weight ratio of 7:3 exhibited enhanced photocatalytic activity relative to that of Pd/TiO_2. This enhancement effect of the Pd–Pt alloy on the photocatalytic performance of the catalyst also shed light on the design of other bimetallic alloy catalysts with enhanced catalytic performance.

Experimental Section

General

All chemicals were from Sigma–Aldrich except P25, which was from Thermal Fisher Scientific (Acros Organics). The catalysts were prepared by a photoreduction reaction. In a typical synthesis, P25 (0.5 g) was dispersed in water (70 mL) in a 100 mL Pyrex glass reactor. Methanol (10 mL) was added to the dispersion as a sacrificial agent. The reactor was sealed and deoxygenated through argon bubbling for 40 min with a flow rate of 100 mL$\,$min^{-1}. The reactor was then illuminated with a 300 W xenon lamp (PE300BF) under magnetic stirring. A solution of H_2PtCl_6 (1.36 mg Pt$\,$mL^{-1}, 1.296 mL) and a solution of $PdCl_2$ (1.36 mg Pd$\,$mL^{-1}, 3.024 mL) was mixed and deoxygenated through argon bubbling in a sealed glass vial, and this solution was injected into the Pyrex reactor by using a syringe pump with a flow rate of 0.1 mL$\,$min^{-1}. The reactor was illuminated for 5 h. After the reaction, the catalyst sample was centrifuged and washed with water until the filtration was neutral in pH. The sample was then dried in a vacuum at 80 °C for 6 h.

Photocatalytic reactions and product analysis

The reaction mixture was prepared by adding photocatalyst (9 mg), substrate (0.1 mmol) and toluene (0.1 mmol, internal standard) in methanol (5 mL). The mixture, in a 10 mL Pyrex glass vial, was sealed and deoxygenated through argon bubbling for 10 min with an argon flow rate of 50 mL$\,$min^{-1}. The mixture was magnetically stirred and irradiated with a 300 W xenon lamp (PE300BF) for 2.5 h at room temperature. The product was analyzed by using an Agilent GC7890A and Shimadzu GCMS-TQ8030 triple quadrupole gas chromatograph mass spectrometer.

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Keywords: hydrogenation · methanol · photocatalysis · reduction · titania

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