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Effect of platinum loading on the photocatalytic activity of cadmium(II) sulfide particles suspended in aqueous amino acid solutions

B. Ohtani [a,*], J. Kawaguchi [a], M. Kozawa [a], Y. Nakaoka [b], Y. Nosaka [b], S. Nishimoto [a]

[a] *Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan*
[b] *Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka 940-21, Japan*

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Abstract

Loading of small amount of Pt by colloid deposition or platinum(IV) oxide (PtO_2) by mechanical mixing onto cadmium(II) sulfide (CdS) particles inhibited the photocatalytic racemization of L-lysine (Lys) in aqueous suspension at ambient temperature under deaerated conditions, but promoted deamino-*N*-cyclization of Lys into pipecolinic acid (PCA). High performance liquid chromatography and gas chromatography–mass spectrometry analyses revealed that oxidation of Lys to release ammonia occurs in parallel with the racemization and PCA formation. The critical amount of the deposits for apparently complete retardation of the Lys racemization depended on whether Pt or PtO_2 was used; a smaller amount of Pt was necessary than of PtO_2, suggesting superior contact of Pt particles with the CdS surface. Transmission electron microscopy analyses supported this. Electron spin resonance measurements of these catalysts revealed that photoexcited electrons move to the Pt site and recombine with positive holes in the absence of an appropriate substrate for oxidation. These findings led to the conclusion that Pt (or PtO_2) deposits act as the reduction site for photoexcited electron in CdS and prohibit a reduction of a surface-adsorbed Lys derivative that is produced through the oxidation with a positive hole.

Keywords: Platinum; Loading; Photocatalytic activity; Cadmium(II) sulfide; Colloid deposition

1. Introduction

Semiconductor photocatalytic reaction is of potential ability for a number of applications, such as energy conversion, organic synthesis or removal of harmful and/or waste chemicals from water or air [1]. Among the many semiconducting materials, titanium(IV) oxide (TiO_2) and cadmium(II) sulfide (CdS) are used widely and successfully in the form of particles or films on substrates. UV (TiO_2) and visible light (CdS) excites them to produce electrons (e^-) and positive holes (h^+), as reductant and oxidant respectively for substrates adsorbed on the surface. In the powder suspension systems, both e^- and h^+ are generated and should be consumed in each particle. Therefore the particle itself works as a small photoelectrochemical cell [2]. This provides a unique characteristic of the photocatalytic reaction as both oxidation and reduction occur in a one-pot reaction without using electrolytes [3], if we can control recombination of e^- and h^+, i.e. shortage of the cell, to a minimum. Several workers have reported examples of such a combined redox process [4–13], e.g. L-lysine (Lys) or its analog undergoes deamino-*N*-cyclization into pipecolinic acid (PCA) by photoirradiated aqueous suspension of TiO_2 or CdS particles [14,15]. In these photocatalytic processes, loading of a small amount, generally less than a few per cent, of noble metals or their oxides as cocatalysts accelerates the reaction and improves the product selectivity [16–19]. During an investigation on the photocatalytic synthesis of PCA from Lys, we found that photoirradiation onto the CdS suspension induces the formation of D-lysine in the absence of a cocatalyst [20], while Pt- or PtO_2-loaded CdS particles exhibit negligible activity for such racemization. It is proved that this photocatalytic racemization is also a combined redox process. This paper describes the detailed study on the effect of cocatalyst on the photocatalytic combined redox processes, racemization and PCA formation, by CdS particles.

2. Experimental details

2.1. Catalysts

Commercial CdS powder (mainly supplied from Furuuchi Chemicals; purity, 99.999%) was used without further acti-

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* Corresponding author.

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vation. X-ray diffraction analysis revealed its crystallite structure of wurtzite (hexagonal system). Fine particles of Pt and PtO_2 were loaded by colloid deposition [15,21,22] and mechanical mixing (shaking) [23,24] respectively. CdS photocatalysts thus obtained were collected on copper microgrids (Oken, type B) from aqueous suspension and observed with a transmission electron microscope (Hitachi H-8000 (175 kV)) [19]. Zinc sulfide (ZnS) and TiO_2 powders were supplied from Nacalai Tesque and Nippon Aerosil respectively.

2.2. Photocatalytic reaction and product analyses

The CdS photocatalyst (50 mg) was suspended in an aqueous solution of Lys (100 μmol; 5.0 cm^3). The suspension was purged of air with an Ar stream and irradiated (at greater than 300 nm) with a 400 W mercury arc (Eiko-sha) at 298 K under magnetic stirring (1000 rev min^{-1}). The details of post-irradiation procedure and analyses were reported elsewhere [15,20]. Gas chromatography–mass spectrometry (GC–MS) analysis was performed with a Shimadzu QP-1000EX equipped with a fused silica capillary. A supernatant solution of photoirradiated reaction mixture was evaporated to dryness, derivatized with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA, Pierce) and subjected to GC–MS analysis. An authentic sample, 6-amino-2-oxahexanoic acid hydrobromide, was prepared according to the literature [25,26]. The assignment of fragment peaks of trimethylsilyl derivatives followed the previous report [27].

2.3. Electron spin resonance measurement

Electron spin resonance (ESR) spectroscopy of photocatalysts was recorded on a JEOL RE-2X spectrometer (X band). Sample powder in a sealed glass tube was irradiated in an ESR cavity with a high-pressure mercury arc (Ushio USH-500D; 500 W, with a 360 nm bandpass filter) at room temperature or at 77 K. A marker of manganese (Mn^{2+}) was used as a reference.

3. Results and discussion

Fig. 1 shows transmission electron micrographs of Pt- or PtO_2-loaded CdS photocatalyst. The base CdS powder consisted of relatively large grains of a few micrometers with roundish edges. Because the thick CdS particles were apparently opaque towards the electron beam in the transmission electron microscope, the observation of loaded Pt or PtO_2 deposits was limited to those located on the fringe of CdS particles. We can see that loose aggregates of Pt particles with an average of a few nanometers cover the CdS particles. On the contrary, PtO_2 particles consisted of rather larger aggregates, which were seldom found on the CdS particles with even 10 wt.% loading. Although we could not observe the whole surface of specimen, because of the above-mentioned limitation, the contact of PtO_2 with CdS seems to be much poorer than that of Pt. The difference between Pt and PtO_2 particles will be discussed later with the results of photocatalytic reaction. Matsumura and Tsubomura [24] have reported similar microscopic micrographs of CdS–Pt prepared by shaking CdS and Pt black powders.

We tried to platinize CdS by impregnation from chloroplatinic acid followed by reduction, as applied to TiO_2 also in this work, but were unsuccessful. This is due to the dark reaction between CdS and chloroplatinic acid in the suspension to yield platinum sulfide. The photocatalytic activity of thus prepared powder was inferior to the original bare CdS powder (data not shown). Therefore, in this study, we used mainly two types of photocatalysts, CdS–Pt and CdS–PtO_2, by colloid deposition and mechanical mixing respectively.

Table 1 shows the representative results of photocatalytic reaction. As reported previously [14], Lys undergoes deamino-*N*-cyclization into PCA, as well as racemization [20]. The latter was recognized by the decrease in enantio excess percentage of L isomer (%ee-L) from the original 100%. CdS- and TiO_2-based photocatalysts give racemic and L-excess PCA respectively, depending on which amino moiety in Lys is oxidized by h^+ in the first step of reaction [14]. CdS oxidizes an α-amino group predominantly as shown in Scheme 1. Bare CdS photocatalysts could promote racemization significantly [20]. Also, bare TiO_2 (P-25) showed a little activity for the racemization, but the rate was much lower than that of CdS particles; Pt loading by impregnation enhanced the consumption of Lys while led to negligible formation of D-lysine. A similar phenomenon was seen for ZnS particles. A commercial ZnS induced the Lys racemization, which was prohibited almost entirely by the PtO_2 loading. These findings suggest that photoirradiated bare semiconductor particles may racemize Lys, although the rate depends strongly on their kind, and that surface modification by noble-metal deposits retards the racemization to result in the enhancement of PCA production. An exception is the case of ZnS which showed markedly lower activity for PCA production with PtO_2 loading. Hereafter, we discuss the photocatalytic reaction by CdS photocatalysts.

It is clear from Table 1 that there should be unidentified product(s) from Lys in the photoirradiated reaction mixture. GC–MS analysis revealed the presence of α-keto acid (**1**), cyclic Schiff base (Δ^1 (or Δ^6)-piperideine-2-carboxylic acid (**2**)) and Δ^2-piperideine-2-carboxylic acid (**3**) in the photoirradiated reaction mixtures. They may be in formation–hydrolysis equilibria of the cyclic Schiff base as well as imine–enamine tautomerism, since nuclear magnetic resonance spectroscopy has proved that a similar compound, Δ^1-piperideine-2,6-dicarboxylic acid, exists in the analogous three forms in water [28]. Abundance of these products depended on the kind of photocatalyst, the reaction conditions, and post-irradiation procedure. The trimethylsilyl derivatives of **2** and **3** were commonly observed in the reaction mixture of photoirradiated CdS and ZnS suspensions. An authentic sample of **1** (or monohydrate of **2**, in the form

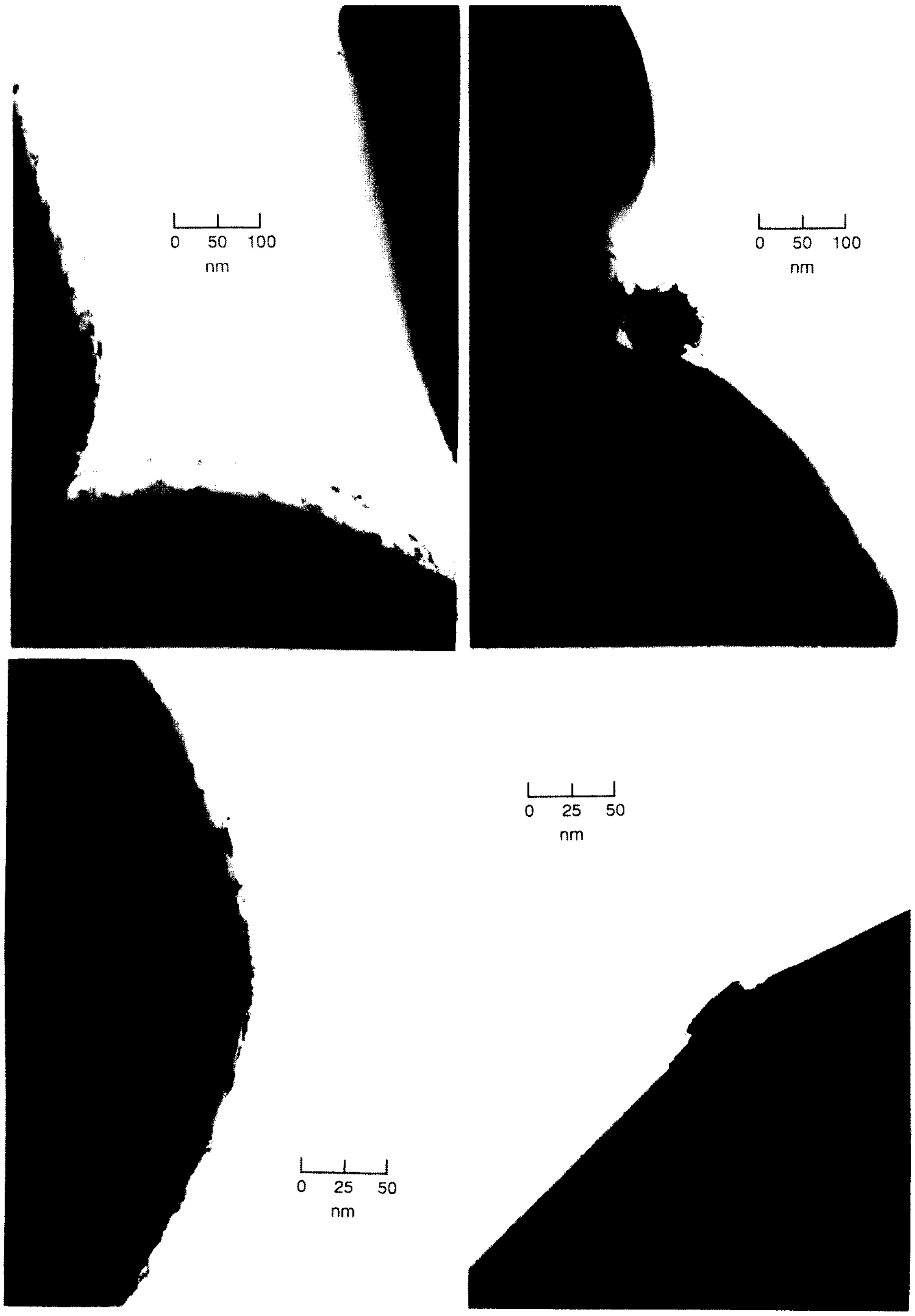


Fig. 1. Transmission electron micrographs of CdS–3 wt.% Pt (left) and CdS–10 wt.% PtO_2 (right).

of hydrobromide) also gave two trimethylsilyl derivatives by the same pre-treatment for GC–MS.

Monotrimethylsilyl derivative of **2**: MS (electron impact (EI)): 199 (M^+), 184 (M^+-CH_3), 156 (M^+-CH_3-CO). MS (CI, isobutane): 200 ($(M+H)^+$).

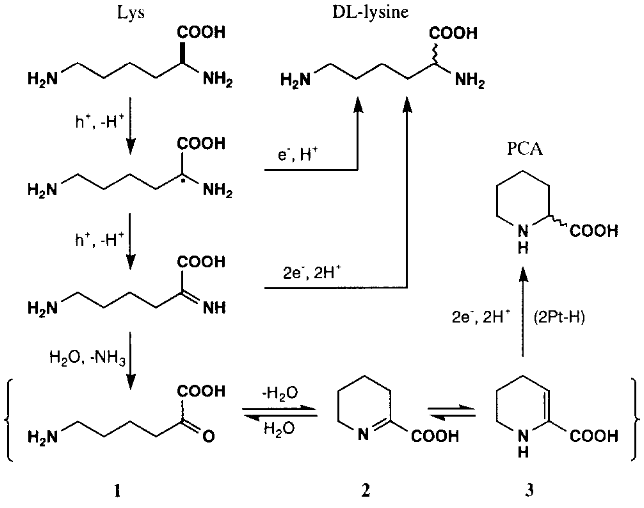
Ditrimethylsilyl derivative of **3**: MS (EI): 271 (M^+), 256 (M^+-CH_3), 228 (M^+-CH_3-CO). MS (CI, isobutane): 272 ($(M+H)^+$). Quantitative analysis of these intermediates could not be achieved mainly owing to its lesser stability. Fig. 2 shows the relation of the molar amount of products other than PCA and that of excess ammonia not accompanied by PCA formation (according to the stoichiometry, Lys = PCA + NH_3). The H_2 yield was also plotted. CdS catalysts loaded with Pt or PtO_2 in various amounts were used in this experiment. It is obvious from this figure that H_2 and NH_3 corresponding to almost 60 and 70% of unidentified product(s) could be recovered. This is consistent with both the stoichiometry,

$$H_2N(CH_2)_4CH(NH_2)COOH + H_2O$$
$$= H_2N(CH_2)_4COCOOH + NH_3 + H_2 \qquad (1)$$

Table 1
Photocatalytic reaction of Lys by suspended semiconductor particles [a]

Run	Catalyst	Irradiation time (h)	H_2 (μmol)	Lysine		PCA	
				Conversion [b] (%)	%ee-L [c]	Yield (%)	%ee-L
1	CdS	24	16	50	76	15	4
2	CdS–2 wt.% Pt	12	55	69	>99	20	2
3	CdS–10 wt.% PtO_2	24	9	79	>99	49	8
4	TiO_2	48	38	33	86	2	–
5	TiO_2–2 wt.% Pt	2	29	90	>99	47	50
6	ZnS	24	122	87	79	47	0
7	ZnS–5 wt.% PtO_2	24	112	47	97	8	15

[a] Catalyst (50 mg) was suspended in an aqueous solution of Lys (100 μmol; 5.0 cm^3) and irradiated under Ar at 298 K with vigorous magnetic stirring.
[b] Apparent conversion of lysine, D and L isomers.
[c] Enantio excess percentage of L isomer in remaining lysine.



Scheme 1.

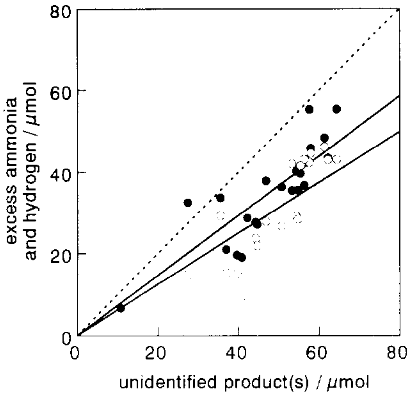


Fig. 2. Molar amounts of excess NH_3 (●) and H_2 (○) as functions of unidentified product(s) from Lys. The data were derived from results shown in Fig. 3.

where α-keto acid is shown representatively, and the GC–MS results. Note that the above plot is independent of the Pt or PtO_2 loading; reaction pathway(s) in these photocatalytic systems is not affected by the loading of metal deposits.

Fig. 3 depicts the change in rates of the above reaction sequences, PCA formation and racemization as well as intrinsic conversion of Lys, as a function of the amount of loading of Pt or PtO_2. Because the apparent conversion of Lys does not include the contribution of racemization, we estimated the intrinsic conversion of Lys as sum of molar amount of D-lysine with that of apparent decrease in L-lysine, on the assumption that racemate formation requires equimolar consumption of Lys according to Scheme 1 [20]. Both figures show a drastic increase in the intrinsic conversion by the Pt or PtO_2 loadings, and the maximum conversion about 2.5 times larger than bare CdS, by almost 0.5 and 3 wt.% loading respectively. Reduction in geminate recombination of e^- and h^+ accounts for this enhancement. On the contrary, the proportion of Lys racemization in the intrinsic conversion decreased drastically to attain to be negligible by 0.3 wt.% (Pt) and 2 wt.% (PtO_2) loadings. The ratio of effective

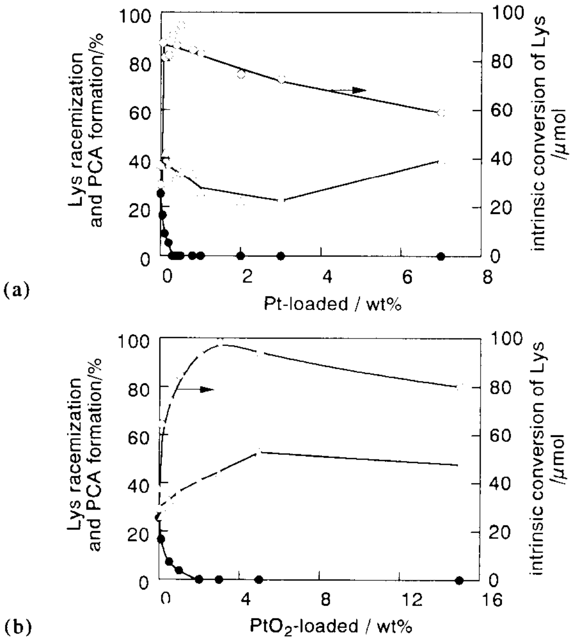


Fig. 3. Dependence of intrinsic conversion of Lys (○), proportion of PCA production (△), and Lys racemization (●) on the amount of (a) loaded Pt and (b) loaded PtO_2. The suspensions were irradiated for 12 h.

loading of Pt and PtO_2 was about 1/6 also in this case. Such a large difference is attributable to the degree of efficient contact of deposits with the CdS surface. As shown by the transmission electron micrographs (Fig. 1), finer aggregates of Pt should have sufficient contact to receive the photoexcited electron generated in CdS, i.e. electrical contact between CdS and Pt is superior to that of PtO_2. These findings suggest that both loadings, Pt or PtO_2, give a same effect in quality, and that the enhancement of Lys conversion and the retardation of racemization are closely linked.

It has also been seen in the other photocatalytic reaction system that the overall reaction rate increases by loading of small amount of Pt (or PtO_2) but decreased with further increment of loading [16,29–31]. It was found that excess loading of Pt onto TiO_2 causes a decrease in photocatalytic activity for Lys conversion and for 2-propanol dehydrogenation [19]. There are several possible reasons for this negative effect of the loadings: the deposits (1) shade the TiO_2 surface from photoirradiation, (2) act as a center for recombination of e^- and h^+, (3) inhibit the surface adsorption of Lys to be oxidized and (4) promote re-reduction of a once-oxidized substrate. The last possibility (4) should not be the case, because this is inconsistent with the present results that the increase of loading prohibited the re-reduction to yield racemate, although we have at present no further experimental evidence to distinguish between the other reasons.

As shown in Scheme 1 and Eq. (1), Lys is oxidized first by h^+ and the resulting intermediate(s) is fated mainly (to be reduced to racemate) to undergo NH_3 release followed by reduction into PCA and to remain unreacted. The inhibition of racemization by Pt (PtO_2) loading in spite of the increase in the oxidized intermediate(s) suggests that the intermediate(s) tends to undergo NH_3 release before the backward reduction in the presence of deposits. Compared with the drastic change in the intrinsic conversion and in the proportion of racemization, PCA formation was less susceptible to the Pt or PtO_2 loading; the behavior was rather complicated, exhibiting a minimum and a maximum respectively, and could not be interpreted. Anyway, it has been proved that Pt (or PtO_2) loading causes the enhancement of Lys oxidation and changes the fate of intermediate(s) drastically.

To determine the behavior of photogenerated species e^- and h^+, ESR spectra of the Pt-loaded and bare CdS photocatalyst were recorded under various conditions (Fig. 4). Although a negligible signal was observed at room temperature under photoirradiation or in the dark, a characteristic signal having $g\parallel = 2.035$ and $g\perp = 2.005$ was found at 77 K for bare CdS particles. The other commercial wurtzite CdS powder under irradiation gave a similar signal and is assigned to a positive hole [32]. It was confirmed that this signal disappeared by loading Lys, as a hole scavenger, on the surface. Aeration of the sample tube reduced the intensity of signals to the extent under deaerated unirradiated conditions, showing that molecular oxygen, presumably adsorbed on the surface, facilitates the recombination of e^- and h^+. Similarly, Pt loading also reduced the intensity of ESR signals. Only 0.05 wt.% Pt loading decreased the intensity to original level before photoirradiation.

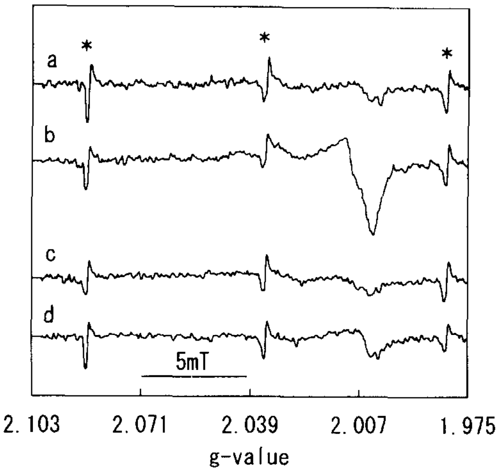


Fig. 4. Parts of ESR spectra of bare and Pt-loaded CdS powders measured at 77 K: curve a, bare CdS in dark; curve b, bare CdS under photoirradiation; curve c, aerated CdS under photoirradiation; curve d, 0.05 wt.% Pt-loaded CdS under photoirradiation; *, Mn^{2+} marker peaks.

From the analogy of a platinized TiO_2 photocatalyst [19], Pt may capture the photoexcited electrons and acts as a cathode for the reduction of proton or other reaction intermediates. In the case of TiO_2, Pt deposits should work as a predominant reduction site, because the bare TiO_2 has a poor ability for reduction of adsorbed substrates other than strong oxidants such as oxygen or silver ions [33]; the photocatalytic activity of bare TiO_2 particles producing PCA and racemizing Lys is negligibly small (Table 1). On the contrary, the CdS surface can be a reduction site evolving H_2 or reducing organic intermediate(s) as seen in Table 1. In both the absence and the presence of Pt, positive holes oxidize Lys adsorbed on the CdS surface to yield surface-bound oxidized intermediate(s). The results of ESR measurement suggest that electrons tend to move to the Pt deposit and recombine with holes in the absence of an appropriate reductant to be oxidized with the holes. Under such conditions, once-oxidized species from Lys (although at present we have no evidence to distinguish whether one- or two-electron oxidation occurs) cannot be re-reduced to result in desorption and/or release of NH_3. Thus the loading of Pt (or PtO_2) separates spatially the sites of oxidation and reduction by h^+ and e^- respectively and therefore allows the occurrence of a chemical reaction, the hydrolysis of intermediate(s) to evolve NH_3 in this case, between the oxidation and the reduction, which makes the photocatalytic reaction irreversible and inhibits the racemization.

4. Conclusions

The effect of the loading of Pt (or PtO_2) has been clarified to be spatial separation of surface reaction sites for oxidation by h^+ and reduction by e^- at the CdS and Pt surfaces respectively. The racemization proceeds by the oxidation of Lys adsorbed on the CdS surface and allowing rapid reduction at the same site before hydrolysis to release NH_3. The loading therefore decreases the racemization as well as geminate recombination of e^- and h^+ to result in the enhancement of overall Lys consumption. Loading of small amount (less than 0.3 wt.%) of Pt by colloid deposition is sufficient for the site separation, while a larger amount of PtO_2 by mechanical deposition is necessary owing to poorer contact with the CdS surface.

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