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Photocatalytic Racemization of Amino Acids in Aqueous Polycrystalline Cadmium(II) Sulfide Dispersions

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L-Lysine in an aqueous solution is partly racemized by photoirradiation (at wavelengths > 300 nm) in the presence of suspended cadmium(II) sulfide particles under a de-aerated atmosphere at room temperature. Loading of a small amount of platinum or its oxide inhibited the racemization, but enhanced *N*-cyclization of L-lysine into DL-pipecolinic acid. ^2H and ^1H NMR measurements of the racemate from photoirradiated reaction mixtures in deuterium oxide solutions revealed the substitution of the α-hydrogen of lysine with deuterium alongside the racemization. These facts suggest a mechanism for photocatalytic racemization that includes both reduction and oxidation by photoexcited electrons and positive holes, respectively. Similarly, the other amino acids, leucine and phenylalanine, undergo photocatalytic racemization under reaction conditions where the α-amino group is deprotonated, although glutamic acid gives no racemate during photocatalytic decomposition. Among the CdS photocatalysts used in this study, well grown cubic crystallites with a specific surface area of *ca.* 8 $m^2\ g^{-1}$ showed the highest selectivity for the racemization of L-lysine.

A recent report from our laboratory revealed that photocatalysis at ambient temperatures by suspended semiconductor particles leads to the deaminocyclization of ω-amino acid into cyclic imino acid; *e.g.* L-lysine and L-ornithine are converted into pipecolinic acid (PCA) and proline, respectively.[1] The optical purity of PCA strongly depends on the photocatalyst; cadmium(II) sulfide (CdS) powders give almost racemic PCA while titanium(IV) oxide (TiO_2) powders afford excess L product. During the investigation of this dependence, we found that racemization of L-lysine also occurs, especially in the aqueous bare CdS suspension. Although several papers have reported other types of photocatalytic isomerizations, geometric[2] or valence,[3] no investigations, to the best of our knowledge, on the photocatalytic racemization of optically active compounds have been described. A mechanism for the photocatalytic racemization of L-lysine, in connection with that for PCA production, and results on the racemization of the other α-amino acids, are presented here. Kinetic information on the reverse reaction, which may occur at the surface of photoirradiated semiconductor particles, but is not detectable in conventional systems involving optically inactive substrates, is also described.

Experimental

Materials

Commercial reagent-grade TiO_2 and CdS powders were used without further purification or activation, unless otherwise stated. The purity was better than 96%, except for the case of CdS from Wako (90%). A CdS pigment supplied from Mitsubishi Materials with unknown purity was prepared by heat treatment in the presence of copper and chlorine. CdS powder was also prepared in our laboratory by mixing solutions of cadmium(II) nitrate and sodium sulfide and subsequent drying. Heat treatment of a commercial CdS (Furuuchi) was made under a nitrogen stream at 1023 K for 2 h in a quartz vessel.[4] The specific surface area of these samples was measured from N_2 adsorption at 77 K following the BET method. Their crystal structure was analysed by X-ray diffraction (XRD) as described elsewhere.[5]

Loading of platinum (Pt; Pt black, Wako) or platinum(IV) oxide (PtO_2; Wako) was achieved by mixing it with CdS powder in a sample tube set on a vibrator.[6] Platinum loading onto TiO_2 powders was made by deposition from Pt sol or impregnation followed by hydrogen reduction. (1) Deposition from sol:[7] A black Pt sol was prepared by refluxing an aqueous solution (150 cm^3) of chloroplatinic acid (H_2PtCl_6, 30 mg) and sodium citrate (0.2%) for 4 h. After cooling, the sol was treated with an Amberlite MB-3 ion-exchange resin in its H^+ and OH^- form for 1 h to remove excess citrate and inorganic electrolytes, and was then filtered. Catalyst powder (0.47 g) was suspended in the resultant Pt colloid (50 cm^3) and then 2.8 g of sodium chloride (NaCl) were added to cause the Pt particles to precipitate. The suspension was stirred for 1 h at room temperature, washed with ion-exchanged water repeatedly and dried *in vacuo*. (2) Impregnation:[8] To an aqueous suspension (500 cm^3) of catalyst (4.9 g) was added dropwise an aqueous solution of H_2PtCl_6 (490 mg). The suspension was evaporated and dried at 383 K for 2 h. The powder was heat treated at 473 K under a continuous H_2 stream (50 $cm^3\ min^{-1}$).

L-Amino acids, their racemates and PCA were products from Ajinomoto or Wako Pure Chemicals and were of the best available grades. Deuterium oxide (D_2O, 99.9 atom% D, Aldrich) was used as solvent for D-incorporation experiments. Ion-exchanged water prepared with a Corning Mega-Pure System MP-190 (> 16 MΩ cm) was used to make the aqueous solutions, unless otherwise indicated.

Photoirradiation and Product Analyses

A suspension of catalyst (50 mg) in an aqueous solution of L-lysine (100 μmol, 5.0 cm^3) was placed in a test tube (18 mm in diameter and 180 mm in length, transparent at > 300 nm) and purged of air by bubbling Ar through it for at least 20 min. The tube was sealed off with a rubber stopper and irradiated at 298 (±0.5) K under vigorous magnetic stirring (1000 rpm) with a 400 W mercury arc (Eiko-sha).

After the irradiation, a portion (200 mm^3) of the gas phase of the sample was withdrawn with a syringe and subjected to GC analysis. The GC analysis conditions were as follows: a

Shimadzu GC8A gas chromatgraph was used, equipped with a thermal conductivity detector (TCD) and a 60–80 mesh molecular sieve 5A column (3 mm in diameter and 3 m in length) with Ar carrier at 373 K for molecular hydrogen (H_2) measurements. A 50–80 mesh Porapak Q column (3 mm in diameter and 3 m in length) was used with helium carrier at 353 K for carbon dioxide (CO_2) analyses. The suspension was centrifuged to remove the catalyst and subjected to HPLC analysis. To separate the enantiomers of lysine and PCA, a portion of the sample solution was treated with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylisothiocyanate (GITC; Wako) 20 min before injection into the HPLC instrument (Shimadzu LC6A) equipped with a UV absorption detector. A mixture of 10 mmol dm^{-3} phosphate buffer and methanol [45 : 55 (v/v)] was made to flow through a reversed-phase column (Cosmosil 5C18-AR; 4.6 mm in diameter and 250 mm in length, Nacalai Tesque) at 1.0 cm^3 min^{-1}. The column temperature was kept at 313 K and eluents were detected at 250 nm. The yield of enantiomers of PCA and D-lysine, as well as of L-lysine, was also measured by HPLC with a Daicel Chiralpak WH column [4.6 mm in diameter and 250 mm in length, at 318 K with 0.5 mmol dm^{-3} aqueous copper(II) sulfate solution]. These HPLC analyses gave almost the same results and, therefore, the former method was mainly used. The conversion and racemate yield of the other amino acids were determined by HPLC using a Daicel Crownpak CR(+) column (4.0 mm in diameter and 150 mm in length) with a diluted perchloric acid (pH 2.0) solution as eluent.

Isolation of products and substrates was performed with five to twelve 5 cm^3 samples obtained under the same conditions. The samples were gathered and loaded onto a column packed with cation-exchange resin (Amberlite IRC-50) equilibrated with a 200 mmol dm^{-3} acetate buffer at pH 4.7. PCA and lysine were eluted with water and an aqueous ammonia solution, respectively. The fractionated eluents were evaporated to dryness, dissolved in D_2O or purified water, and subjected to NMR measurements. ^1H and ^2H NMR spectra were recorded on JEOL GSX 270 (270 MHz) and Nicolet NT-300 instruments with a 1280 data processor (46 MHz), respectively. In both measurements, a contaminated HDO signal was used as an internal standard for the chemical shift {4.76 ppm downfield from sodium [$^2H_4$]trimethylsilylpropionate (TSP)}. Aniline hydrochloride was added as an H content internal standard in the ^1H NMR measurements.

Results and Discussion

Photocatalytic Racemization of L-Lysine

Photoirradiation of the suspension of CdS in an aqueous solution of L-lysine led to the formation of PCA under an argon atmosphere at 298 K (Table 1) as reported previously.[1] Both in the presence and absence of platinum(IV) oxide (PtO_2), almost racemic PCA was obtained, presumably through a pathway involving the oxidation of the α-amino group, but not the ε-amino group, by a photogenerated positive hole (h^+) in the first stage of reaction (Scheme 1; this shows the reaction mechanism in D_2O suspension, and here all D should read as H).

The PtO_2 loading onto CdS gave rather higher activity for PCA production from L-lysine[1] than loading with fine platinum (Pt) black particles (data not shown). Racemization of L-lysine was also observed, particularly with bare CdS powders (Table 1, entries 1–3). Control experiments in the dark or irradiation without CdS induced no racemization, suggesting that the racemization is caused by photocatalysis by suspended semiconductor particles, *i.e.* primarily by the photoexcited electron (e^-) and h^+. The photocatalytic production of racemic PCA by CdS particles, as described above, is not attributable to this L-lysine racemization and subsequent *N*-cyclization, because some kinds of CdS powders were not so active towards racemization but produced racemic PCA, as shown in Table 1. For example, CdS powders loaded with PtO_2 gave racemic PCA while lysine remaining in the reaction mixture was negligibly racemized.

Powders of TiO_2 loaded with Pt gave practically no racemic lysine (entries 6 and 7); D-lysine could not be detected in the photoirradiated suspension of TiO_2–Pt. The Pt-loaded TiO_2(P) (Degussa, entry 6) was quite active, consuming L-lysine almost completely during the 4 h irradiation and giving PCA selectively. It remains a possibility that L-lysine was racemized in the TiO_2 suspension but consumed thereafter. However, during the course of the reaction practically no D-lysine could be seen (data not shown). Since L-lysine consumption was negligible in the absence of Pt, we could not confirm the ability of bare TiO_2 powders (from Merck and Degussa) to photocatalyse the racemization.

The selectivity for the photocatalytic racemization was evaluated as the molar ratio of the racemate yield to intrinsic conversion, the latter of which is the sum of the consumption

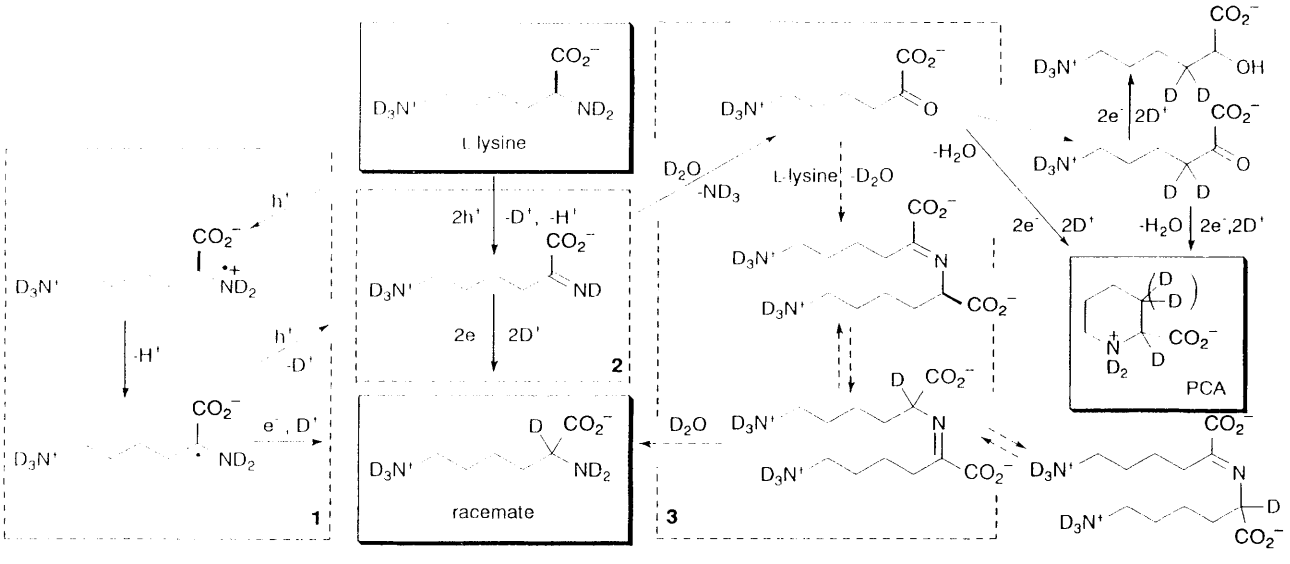

Table 1 Photocatalytic reaction of L-lysine in an aqueous suspension of semiconductor particles[a]

					lysine content[c] (%)					PCA content[c] (%)		
entry	catalyst[b]	irradiation time/h	H_2 content /μmol	CO_2 content /μmol	L	D	racemate chemical yield[c] (%)	selectivity[d] (%)	α-D chemical yield[e] (%)	L	D	L-enantiomer excess (%)
1	CdS(F)	12	2	<0.1	75	4	8	27	—	6	5	9
2	CdS(K)	12	4	<0.1	56	14	28	48	—	4	3	14
3	CdS(K)	24	12	<0.1	28	17	34	38	—	8	7	6
4	CdS(F)–PtO_2[f]	12	14	3	39	1	2	3	—	18	16	5
5	CdS(K)–PtO_2[f]	12	55	5	16	1	2	2	—	13	13	<0.1
6	TiO_2(P)–Pt[g]	4	22	<0.1	1	<0.1	<0.2	<1	—	56	17	53
7	TiO_2(M)–Pt[h]	6	19	<0.1	36	<0.1	<0.2	<1	—	26	7	57
8	CdS(K)	23[i]	2	<0.1	43	24	48	59	50	5	5	<0.1
9	CdS(K)–PtO_2	8[i]	31	<0.1	36	1	2	3	3	12	12	<0.1

[a] Catalyst (50 mg) was suspended in an aqueous solution (5 cm^3) of L-lysine (20 mmol dm^{-3}) and irradiated at 298 K under an argon atmosphere. [b] CdS(F) and CdS(K) were supplied from Furuuchi and Katayama Chemicals (96%), respectively. TiO_2(P) and TiO_2(M) refer to TiO_2s from Degussa (P-25) and Merck, respectively. [c] Based on L-lysine in feed (100 μmol). [d] Selectivity for the photocatalytic racemization: [racemate yield]/([intrinsic conversion] = [racemate yield] + [apparent conversion]). [e] Yield of lysine substituted with deuterium at the α-position based on feed (100 μmol). [f] 10 wt.%. [g] 2 wt.%, by impregnation. [h] 0.8 wt.%, by deposition from Pt sol. [i] D_2O was used as solvent instead of purified water.

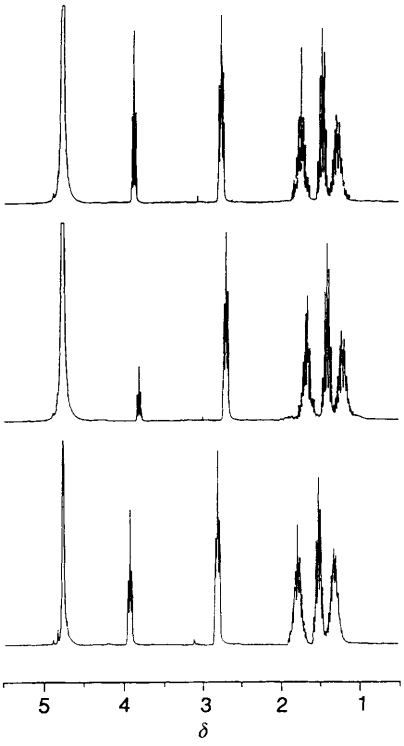

Fig. 1 Portions of the ^{1}H NMR spectra of lysine hydrochloride in the feed (lower) and recovered from the mixture photoirradiated in the presence of CdS(K) (middle) and of CdS(K)–PtO_2 (upper). Assignment of peaks: 1–2 ppm δ-, γ-, ε-Hs; 2.7–2.8 ppm, β-Hs; 3.8 ppm, α-H; and 4.76 ppm, HDO.

of the starting amino acid and the racemate yield, results are listed in Table 1. The higher selectivity of CdS(K) and its reduction by loading with PtO_2, can be clearly seen. An inverse relationship between the selectivity and the H_2 yield was also observed. This may be due to the formation and retention of intermediate species, presumably keto acid (Scheme 1), a precursor of PCA; keto acid formation requires only h^+, and the corresponding e^- is used for H_2 production at the Pt (PtO_2) surface unless utilized for PCA production.

^{1}H NMR spectra (Fig. 1) of partly racemized lysine isolated from the photoirradiated reaction mixture revealed that the ^{1}H content at the α-carbon (3.8 ppm downfield from TSP) was markedly reduced by the photocatalytic reaction in deuterium oxide (D_2O) (entries 8 and 9). On the other hand, the other positions seem to undergo negligible change in ^{1}H content, but this could not be confirmed from the ^{1}H NMR charts owing to some experimental error in the integration of the peaks. The incorporation of D atoms only at α positions was clearly shown by ^{2}H NMR spectroscopy (Fig. 2); the

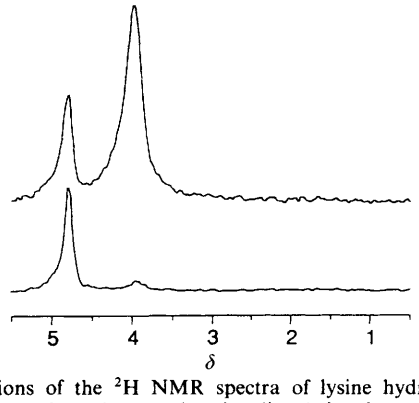

Fig. 2 Portions of the ^{2}H NMR spectra of lysine hydrochloride recovered from the mixture photoirradiated in the presence of CdS(K) (upper) and of CdS(K)–PtO_2 (lower). The assignment of peaks is identical to that in Fig. 1.

appearance of an α-D signal (3.8 ppm) was observed, as well as the contaminated HDO signal (*ca.* 4.8 ppm).

In accord with the fact that CdS catalysts loaded with PtO_2 are less active for racemization, the D-atom content at the α-position of lysine in a CdS-PtO_2 suspension (entry 9) was much lower than that in the presence of bare CdS (entry 8). Thus, α-H is selectively substituted with D through the photocatalytic racemization. Photoirradiation of a mixture of D_2O, an α-amino acid and CdS may be a facile method of direct deuterium (or tritium, if tritium-containing water is used instead of D_2O) substitution at the α-position, with unavoidable racemization.

Mechanism

To interpret the photocatalytic racemization, three reaction pathways are plausible (Scheme 1). (1) L-Lysine undergoes one-electron oxidation to the cation radical (or the radical if accompany by H^+ release) and successive reduction to the original, but optical inactive, DL-lysine. (2) L-Lysine undergoes two-electron oxidation to an α-imine and successive reduction to the racemate, before hydrolysis to form an α-keto acid and ammonia. (3) The keto acid and/or the α-imine is condensed with lysine. The carbon–nitrogen double bond migrates and hydrolysis occurs to form lysine and the keto acid. The third pathway is similar to the mechanism known as transamination,[9] but can be ruled out, because neither consumption nor racemization of L-lysine could be observed in an unirradiated aqueous CdS suspension in the presence of a keto acid, pyruvic acid. Further evidence to support the elimination of pathway 3 is that almost no deuteriation at the β-position of the remaining lysine was observed in D_2O solution, while more than 70% of the isolated PCA, produced through the same keto acid (and/or α-imino acid) intermediate, were D-substituted at the β-position, presumably through keto–enol tautomerism, as shown in Scheme 1. In the photocatalytic reaction in D_2O, the first two pathways should produce α-D substituted racemate, *i.e.* a molar amount of racemate is equal to the amount of α-D substituted lysine. Apparent experimental data both in the absence and presence of PtO_2 (Table 1), *i.e.* a percentage yield of racemate almost equal to that of α-D substituted lysine, confirm that the reaction mechanism involves either the first or second pathway, although we have no information to distinguish them. Anyway, the photocatalytic racemization continues through a combined process of oxidation by h^+ and reduction by e^-, as has been shown in the photocatalytic *N*-alkylation of amines and ammonia.[1,10]

Photocatalytic Racemization of the Other Amino Acids

Table 2 shows the results of photocatalysis by suspended CdS particles of the reactions of a variety of amino acids. Except for L-glutamic acid (Glu), photocatalytic racemization of these amino acids was commonly observed.

Again, as seen for the Lys solution, neither racemization nor consumption of these amino acids could be detected in the absence of the catalysts, even with the addition of an equimolar amount of sodium hydroxide. Therefore neutral alkyl (L-leucine; Leu) and neutral phenyl-group-containing (L-phenylalanine; Phe) amino acids, as well as the basic amino acids (Lys), undergo photocatalytic racemization, indicating that CdS-induced photocatalytic racemization is applicable to amino acids in general.

Note that the photocatalytic conversion of Glu (although no racemization was seen) required the addition of twice the molar amount of alkali, NaOH, while the other amino acids react in the presence of equimolar amounts of NaOH; a neg-

Table 2 Photocatalytic reaction of amino acids in an aqueous dispersion of CdS particles in the presence and absence of platinum or platinum oxide co-catalyst[a]

entry	amino acid[b]	catalyst[c]	H_2 content/μmol	substrate (%)[d] L	substrate (%)[d] D	racemate chemical yield[d] (%)	conversion[e] (%)	selectivity[f] (%)
1	Leu	CdS(K)	4.1	46	23	46	31	60
2	Leu	CdS(K2)	0.1	69	13	26	18	60
3	Leu	CdS(F)	2.8	79	10	20	11	65
4	Leu	CdS(K)–Pt[g]	8.5	57	16	32	27	54
5	Phe	CdS(K)	2.9	48	27	54	25	68
6	Phe	CdS(K2)	<0.1	77	13	27	9	75
7	Phe	CdS(F)	1.7	91	5	10	4	71
8	Phe	CdS(K)–Pt[g]	8.5	59	13	26	28	48
9	Glu	CdS(K)	4.8	56	<0.1	<0.2	44	<1
10	Glu	CdS(K2)	<0.1	88	<0.1	<0.2	12	<1
11	Glu	CdS(F)	1.3	87	<0.1	<0.2	13	<1
12	Glu	CdS(K)–Pt[g]	9.0	71	<0.1	<0.2	29	<1
13	Glu	CdS(K)–PtO_2[h]	13	59	<0.1	<0.2	41	<1

[a] Catalyst (50 mg) was suspended in an aqueous solution (5 cm^3) of amino acid (20 mmol dm^{-3}) and irradiated for 40 h at 298 K under an argon atmosphere. [b] Leu, Phe and Glu indicate L-leucine, L-phenylalanine and L-glutamic acid, respectively. [c] CdS(K2) was supplied from Katayama Chemicals (99.99%). The other abbreviations are identical to those in Table 1. [d] Based on L-lysine in the feed (100 μmol). [e] Apparent conversion of amino acid. [f] Selectivity for the photocatalytic racemization: [racemate yield]/([intrinsic conversion] = [racemate yield] + [apparent conversion]). [g] 2 wt.%. [h] 5 wt.%.

ligible amount of Glu was consumed with a molar equivalent of NaOH. These facts can be interpreted in terms of the protonation–deprotonation equilibrium of the α-amino groups. The addition of an equimolar amount of NaOH to an aqueous solution of Leu or Phe induces the deprotonation of the α-ammonium group to form an amino acid anion, as follows.

$$RCH(NH_3^+)CO_2^- + OH^- \rightarrow RCH(NH_2)CO_2^- + H_2O \quad (1)$$

In the case of Lys, the α-amino group is also deprotonated, similar to the above structure, under the present reaction conditions, because of its smaller pK_a, *i.e.*, lower basicity of the α-amino group ($pK_a = 9.06$) than of the ε-amino group ($pK_a = 10.54$).[11] On the other hand, for the deprotonation of the α-amino group in Glu, two carboxylic acids have to be neutralized using twice the molar amount of NaOH; *i.e.* the amino group in Glu may still be in the ammonium form upon addition of equimolar amounts of NaOH. Thus, the photocatalytic conversion of the amino acids by the CdS dispersion seems to require the deprotonation of the α-amino group.

As shown in the preceding section, the first step of photocatalytic racemization is the oxidation of the α-amino group by an h^+ of CdS. Since the deprotonation of the ammonium group may decrease the oxidation potential, *i.e.* make oxidation more feasible, one possible reason for the above requirement could be the energetics of the photoinduced oxidation step. The upper edge potential of the valence band in CdS is reported to be +1.6 V (*vs.* NHE, at pH 7), which is rather higher than that of TiO_2 (2.6 V).[12] The oxidizing ability of the positive holes in CdS towards the ammonium group is, therefore, lower than that of TiO_2. In fact, predominant formation of racemic PCA from the Lys in CdS suspension may be caused by the favourable oxidation of the α-amino group rather than that of the ε-ammonium moiety in Lys, while TiO_2 seems to oxidize both amino groups.[1]

The reason for the negligible racemization of Glu is not known at present. The negative charge at the ω-carboxylate may influence the structure of the surface-adsorbed substrate and/or intermediate(s) and thereby the electron (or positive hole) transfer. Under the conditions with twice the molar amount of NaOH, Glu may undergo oxidation at the α-amino group followed by decarboxylation of the adjacent carboxylate, before back electron transfer to yield the racemate (see Scheme 1), although we have no experimental evidence for such oxidized carboxylated product(s).

The platinization of CdS influenced the photocatalytic activity for racemization and conversion, as can also be seen in Table 2; a slightly lower selectivity was observed for racemization along with an increase in the H_2 yield. Since the surface of Pt is known to be a good hydrogen production site, it is possible that the photoexcited electrons move to the Pt through the CdS/Pt interface and produce hydrogen atoms which then form H_2. This decreases the efficiency for reduction of the once oxidized amino acid, *i.e.* increases the lifetime of the intermediate species which undergo further oxidation or deamination (of the radical cation and imine in Scheme 1, respectively). In other words, loading with Pt would separate the sites for oxidation and reduction by h^+ and e^-, respectively. In contrast to the TiO_2 photocatalyst,[13] the CdS surface itself can serve as an H_2 evolution site. Therefore, the effect of loading of co-catalyst is not so drastic. The change in the racemization selectivity of Lys with the variation in Pt loading has been studied (data not shown); increases in the loaded amount of Pt (or PtO_2) reduced the selectivity to almost zero. A detailed study of the physical properties of the Pt-loaded CdS photocatalyst is now under way and will be reported elsewhere.[14]

Photocatalytic Activity of CdS Powders

Fig. 3 shows the rates of L-lysine racemization and PCA formation by various CdS powders. The first five CdS samples consist of well grown (specific surface area of <15 m^2 g^{-1}) wurtzite (hexagonal) crystallites, the middle four samples of well grown sphalerite (cubic) ones, and last four samples of poorly grown (specific surface area of >50 m^2 g^{-1}) cubic ones.

Although product(s) have not been identified yet, the keto acid and/or an α-hydroxy acid (Scheme 1), produced through reduction of the keto acid, are most likely from several experimental results. The catalyst obtained by annealing a commercial CdS sample (Furuuchi) showed the highest activity for photocatalytic conversion of lysine and formation of PCA.[15] The CdS powder was originally hexagonal in structure and retained the same crystallite morphology although

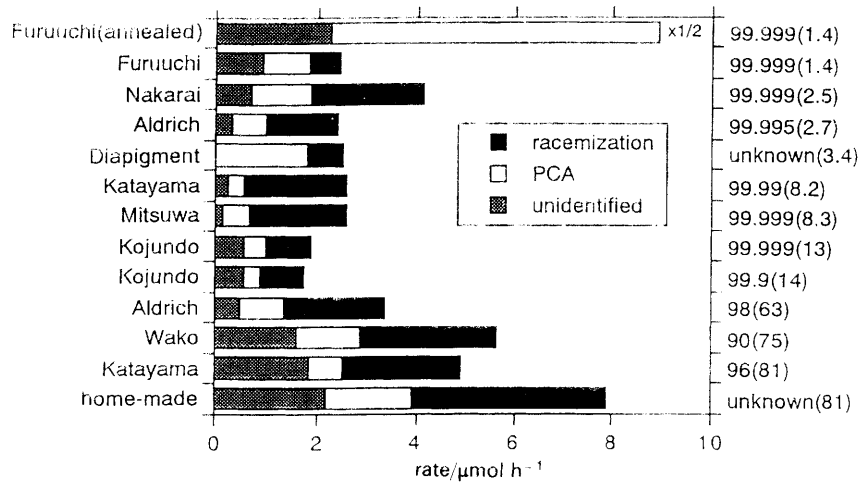

Fig. 3 Rate of photocatalytic reaction of Lys in an aqueous suspension of CdS particles. Data were calculated from the results for 2–12 h irradiations depending on the rate of each catalyst. Figures on the right-hand side refer to the percentage purity of CdS and those in parentheses to the specific surface area (in $m^2\ g^{-1}$). Rates for unidentified product(s) were calculated from the differences between the rates of total consumption of L-lysine and of production of the identified products.

somewhat larger, even after the heat treatment. Similarly, a higher photocatalytic activity has been reported for this CdS powder in H_2 production from aqueous sodium sulfite solution.[16]

Although the rate is slow, the highest selectivity (>70%) for L-lysine racemization is obtained from CdS powders supplied from Katayama (99.99% purity) and Mitsuwa, both of which consist of well grown crystallites of cubic structure with a specific surface area of around 8 $m^2\ g^{-1}$. However, similar CdS powders from Kojundo Chemicals with well grown cubic crystallites showed a moderate selectivity of *ca.* 50%. Therefore, the bulk, *i.e.* the crystallite, structure of CdS is a less decisive factor in the racemization. This is quite reasonable because efficient utilization of both h^+ and e^- by surface-adsorbed amino acid is necessary for the photocatalytic racemization, which is therefore sensitive to the surface properties. Fig. 4 is a plot of selectivity and rate of racemization as a function of the specific surface area of the CdS photocatalyst.

The rate seems to increase with the surface area and this can be attributed to the increase in the amount of surface-adsorbed substrates, *i.e.* amino acid. This also induces an enhancement in the formation of other products, *e.g.* PCA, to result in a moderate selectivity of *ca.* 50%. For lower surface areas, $<20\ m^2\ g^{-1}$, the behaviour was complicated and it is difficult to interpret the photocatalytic activity in terms of the surface area alone. The molecular structure of the adsorbed amino acid and/or electronic structure of the surface sites

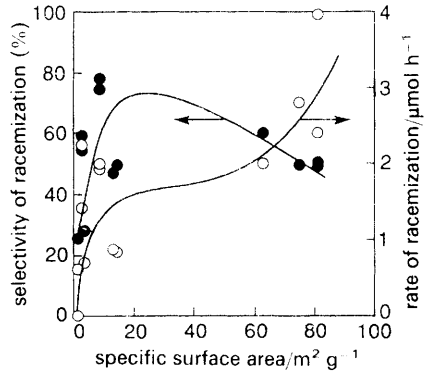

Fig. 4 Selectivity (●) and rate (○) of photocatalytic racemization of L-lysine as a function of specific surface area of the CdS powders

would have a significant effect on the photocatalytic racemization. Research on this topic is in progress.

Photocatalytic Racemization as a Proof of the Reverse Reaction

Note that the total photocatalytic activity is underestimated if DL-lysine is used as a starting material, *e.g.* in the case of Katayama (99.99%) CdS, only a quarter of the activity is observed as DL-lysine consumption (0.6 mmol h^{-1}), although most of the e^- and h^+ take part in an undetectable chemical reaction, *i.e.* racemization (2.0 mmol h^{-1}). The quantum efficiency of the semiconductor photocatalytic reactions could be lowered by recombination of e^- and h^+ and/or the reverse reaction induced by reduction/oxidation of once oxidized/reduced intermediates. The photocatalytic racemization reported here is direct evidence of the latter and suggests that such a reverse reaction probably occurred in the photocatalysis of optically inactive substrates, *e.g.* propan-2-ol or ethanol.

Conclusion

In conclusion, the mechanism of the photocatalytic racemization of L-lysine in aqueous solution has been clarified to be a redox-combined process on the surface of photoirradiated CdS particles. Improvement of the catalysts and conditions for more efficient racemization and position-selective deuteriation of amino acids is under way. Although racemization of optically active compounds is essentially a down-hill reaction and less significant for organic syntheses, it is sometimes required in industrial and/or laboratory processes, especially to convert less valuable enantiomers into the more valuable isomer. The results presented here may be a starting point for a novel procedure of racemization and position-selective deuteriation of amino acids.

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