

A Hollow Core-Shell Silica-Titania Photocatalyst for Efficient Stereoselective Synthesis of Pipecolinic Acid

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INTRODUCTION

One of the approaches for photocatalytic selective organic synthesis is utilization of photocatalysts of or in defined microstructures; TiO₂ particles or isolated titanium oxide species are distributed onto or into inorganic supports. We have reported^{1,2} fabrication of a novel core-shell composite photocatalyst which consisted of commercially available TiO₂ particles incorporated in a hollow silica shell (SiO₂/void/TiO₂). The composite possesses size-selective properties in the photodecomposition of organic compounds; SiO₂/void/TiO₂ showed photocatalytic activity for decomposition of small substrates retaining the activity of original bare TiO₂, while negligible activity for polymers was observed, i.e., SiO₂/void/TiO₂ exhibits molecular size selectivity. Recently, we have attempted to use the SiO₂/void/TiO₂ photocatalyst for the synthesis of L-pipecolic acid (L-PCA), a useful intermediate material for various fine chemicals,³ and found another function of silica shell to improve stereoselectivity, instead of molecular-size selectivity and report here.^{4,5}

EXPERIMENTAL

Preparation of SiO₂/void/TiO₂ was performed by coating of TiO₂ (Ishihara Sangyo ST-41) with a carbon layer and a silica layer followed by heat treatment to remove the carbon layer, as shown schematically in Fig. 1(a).^{1,2} As a reference, TiO₂ mechanically mixed with silica (Wako; *mec*-SiO₂+TiO₂) and TiO₂ directly coated with silica (*dir*-SiO₂/TiO₂) were also prepared. Since platinum (Pt) deposits on the TiO₂ surface are required for the photocatalytic synthesis of L-PCA,³ all samples were platinized (2wt%) using two-step photodeposition method.

For the photocatalytic reaction of redox-combined stereoselective synthesis of L-pipecolic acid (L-PCA) from L-lysine (L-Lys), a Pt-loaded photocatalyst (0.05 g as TiO₂) was suspended in an aqueous solution (5.0 cm³) containing L-Lys (100 μmol) and photoirradiated by a high-pressure mercury arc (Eiko-sha, 400 W) under argon (Ar) with magnetic stirring (1000 rpm) at 298 K. The yield of enantiomers of PCA, as well as the amount of unreacted L-Lys, was measured by HPLC (Shimadzu LC-6A equipped with a Daicel Chiral-Pak MA(+) column and an ultraviolet absorption detector).

RESULTS AND DISCUSSION

Table 1 summarizes the results for the synthesis of L-PCA from L-Lys by 2-h photoirradiation using various platinized TiO₂ photocatalysts. Photoirradiation of the TiO₂ photocatalysts suspended in an aqueous solution of L-Lys under Ar led to the formation of PCA, as reported previously.³ Complete consumption of L-Lys was achieved using TiO₂ and also *mec*-SiO₂+TiO₂. These photocatalysts showed very similar results in terms of selectivity (S_{PCA}), optical purity (OP_{PCA}) and the rate of PCA formation (R_{PCA}), suggesting that the mechanical mixing of silica with TiO₂ does not give any effect on this reaction as only the TiO₂ part was responsible for the photocatalytic reaction. As expected, *dir*-SiO₂/TiO₂ showed poor photocatalytic activity to convert only 14% of L-Lys, thus proving that direct coverage of the TiO₂ surface with silica hinders the activity of the TiO₂ by

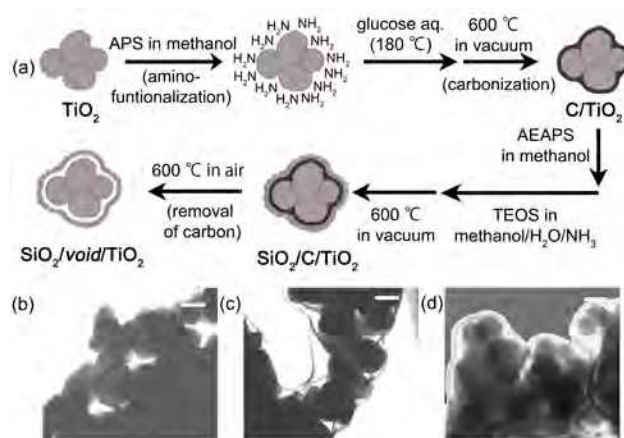


Figure 1. (a) Schematic representation of the procedure for preparation of SiO₂/void/TiO₂, SEM image taken in transmission mode for (b) TiO₂, (c) SiO₂(0.5)/void/TiO₂ and (d) SiO₂(0.5)/void/TiO₂ after deposition of Pt particles. Scale bar corresponds to 100 nm.

Table 1. Synthesis of PCA from L-Lys using various platinized TiO₂ photocatalysts.

photocatalyst	conversion (%)	S _{PCA} ^a (%)	OP _{PCA} ^b (%)	R _{PCA} ^c	Y _{H₂} ^d /μmol
TiO ₂	100	51	57	27	75
<i>mec</i> -SiO ₂ +TiO ₂	100	52	59	27	63
<i>dir</i> -SiO ₂ /TiO ₂ ^e	14	26	- ^f	0.2	2
SiO ₂ (0.5)/void/TiO ₂	98	43	70	22	72
SiO ₂ (1.5)/void/TiO ₂	96	50	70	25	50
SiO ₂ (3.0)/void/TiO ₂	96	46	70	23	57

^aSelectivity of PCA production based on amount of consumed L-Lys.

^bOptical purity of L-PCA. ^cRate of PCA formation in the unit of μmol h⁻¹. ^dYield of H₂. ^ePlatinization via photodeposition was unsuccessful (see text). ^fNot determined.

prohibiting Pt deposition as well as L-Lys adsorption onto the bare TiO₂ surface. The SiO₂(0.5)/void/TiO₂ particles prepared with 0.5 h of silylation period showed the performance almost the same as that of bare TiO₂. Although the selectivity was slightly lower than that of bare TiO₂, SiO₂/void/TiO₂ exhibited the highest OP_{PCA}, 13% more than that of platinized bare TiO₂, among all the samples. In order to further prove the effectiveness of the hollow core-shell structure, SiO₂/void/TiO₂ with thicker layer of silica shell were also prepared, by extending the silylation period (1.5 h and 3.0 h). The thickness of the silica layer was increased to 14–32 nm and 28–45 nm, respectively, from 9–10 nm for SiO₂(0.5)/void/TiO₂. While SiO₂(1.5)/void/TiO₂ exhibited the best performance among the tested samples, it seemed that the photocatalytic performance (conversion, S_{PCA}, OP_{PCA} and R_{PCA}) was almost independent of the silica shell thickness. This suggests that the silica shell behaves as highly porous optically transparent penetration-free layer which surrounds the TiO₂ core and that this swollen sponge-like silica layer controls the stereoselectivity of the reaction.

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