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Immobilization of CdS nanoparticles formed in reverse micelles onto aluminosilicate supports and their photocatalytic properties

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Abstract

CdS nanoparticles, prepared in reverse micellar system, were immobilized onto thiol-modified aluminosilicate particles (AS–SH) by a simple operation: addition of AS–SH in the micellar solution and mild stirring. The resulting CdS nanoparticles–aluminosilicate composites (AS–CdS) were used as photocatalysts for H_2 generation from 2-propanol aqueous solution. The chemical properties of the aluminosilicate, such as affinity for water and other reactants, were found to affect the photocatalytic property of the CdS nanoparticles immobilized. Zeolite particles, having affinity for water and 2-propanol, gave a good AS–CdS photocatalyst with respect to H_2 generation.

Keywords: CdS nanoparticles; Aluminosilicate support; Photocatalyst; Hydrogen generation

1. Introduction

In recent years a large number of techniques have been developed to prepare nanoparticles. Among these techniques, precipitation in the reverse micellar system has been expected to be a useful methodology for the production of nanoparticles, such as CdS nanoparticles [1–7]. The nanoparticles thus prepared need to be recovered from reverse micelles and immobilized onto stable supports, in order to be utilized as catalysts and photocatalysts essentially. In the previous work, we reported on the immobilization of CdS nanoparticles formed in reverse micellar systems onto thiol-modified alumina particles [8]. This is one of the most attractive and simple methodologies for the direct recovery and immobilization of nanoparticles, such as CdS nanoparticles, using 3-mercaptopropylmethyldimethoxysilane (MPDMS)-modified alumina particles (Al_2O_3–SH) via chemical bonding by the addition of the supports into the reverse micellar solution under conditions of mild stirring. The CdS nanoparticles immobilized on Al_2O_3–SH were effectively stabilized against photoirradiation, than the CdS nanoparticles on the other supports such as SiO_2–SH. In the present work, the further study on the effect of metal oxide supports on the photocatalytic properties for the CdS nanoparticles was carried out by using several types of thiol-modified aluminosilicate particles (AS–SH).

2. Experimental

2.1. Preparation of thiol-modified aluminosilicate supports (AS–SH)

Aluminosilicates (AS) and Al_2O_3 used in this study are shown in Table 1. Mesoporous aluminosilicate MSU–S was prepared via a procedure similar to that reported by Liu et al. [9,10]. $Al_2O_3{\cdot}3SiO_2$ and Al_2O_3 were supplied by Wako Pure Chemical Industries, Ltd. Zeolite 320 (Z320) and 331 (Z331) were supplied by Tosoh Corporation. The modification of the supports with thiol group was carried out using a thiol functionalized alkoxysilane 3-mercaptopropylmethyldimethoxysilane (MPDMS), as reported previ-

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Table 1
Properties of aluminosilicate and Al_2O_3 supports

Support	Particle size (μm)	Specific surface area (m^2/g)	Quantity of NH_3 adsorbed (mmol/g)	Quantity of –SH (mmol/g)	Quantity of CdS immobilized (μmol/g)
MSU–S	34.90	411.5	0.39	0.95	44.69
$Al_2O_3{\cdot}3SiO_2$	13.00	493.5	0.87	0.96	54.19
Z320	6.22	455.5	0.43	0.99	51.39
Z331	1.66	535.8	1.71	0.98	38.47
Al_2O_3	80.70	129.2	0.05	1.18	66.16

ously for Al_2O_3 [8]. The aluminosilicate (4 g) was refluxed in 100 ml of toluene with 5 ml MPDMS at 373 K for 24 h under N_2 atmosphere. After cooling, the solid product was filtered off, washed with hot toluene to ensure complete removal of the unreacted MPDMS and finally dried in vacuo. The resulting thiol-modified aluminosilicates (AS–SH) and Al_2O_3 are denoted henceforth as MSU–S–SH, $Al_2O_3{\cdot}3SiO_2$–SH, Z320–SH, Z331–SH, and Al_2O_3–SH.

2.2. Preparation and immobilization of CdS nanoparticles

CdS nanoparticles were prepared in reverse micellar systems consisting of sodium bis(2-ethylhexyl)sulfosuccinate (AOT; supplied by Tokyo Chemical Industry, Ltd.; 0.1 mol/L), water, and isooctane (2,2,4-trimethylpentane). A quantity of 50 ml of AOT–isooctane reverse micellar solution of water content W_o $(=[H_2O]/[AOT]) = 6$, containing 0.2 mmol/L $Cd(NO_3)_2$, was added rapidly to a second micellar solution (50 ml) of the same W_o containing 0.2 mmol/L Na_2S, and stirred vigorously by magnetic stirrer at 298 K in a glass vessel. Ten minutes after the mixing of the two solutions, 0.05 g of AS–SH or Al_2O_3–SH was added to 100 ml of the reverse micellar solution, stirred for 24 h, and separated by centrifugation. The resulting composite particles are denoted henceforth as MSU–S–CdS, $Al_2O_3{\cdot}3SiO_2$–CdS, Z320–CdS, Z331–CdS, and Al_2O_3–CdS.

2.3. Analysis

The particle size for the aluminosilicates and Al_2O_3 supports was measured by a laser scattering particle size distribution analyzer (Horiba LA-910W). The specific surface area for the supports was measured by BET method, using N_2 adsorption at 77 K (Bel Japan Inc. Belsorp 18Plus-SP). The amount of adsorbed NH_3 on the supports was measured volumetrically at 273 K using a MKS Baratron type 627 absolute pressure instrument. The amount of strongly adsorbed NH_3 was estimated from the difference of the first and second isotherms at equilibrium pressures. The second isotherm was obtained after the NH_3-covered sample was degassed at 353 K. The quantity of thiol group on the supports was determined by iodometric titration. The absorption spectra for the CdS nanoparticles in the reverse micellar solution were recorded by a diode-array UV–visible spectrophotometer (Hewlett–Packard 8452A). The diffuse reflectance spectra for the CdS nanoparticles immobilized on the supports were recorded, following dispersion of the composites into the aqueous solution, using a UV–vis spectrophotometer (Japan Spectroscopy V-550) equipped with an integrating sphere attachment (ISV-469). The quantity of CdS immobilized onto the supports was determined by ICP-AES (Nippon Jarrell-Ash ICAP-575 Mark II) following dissolution of CdS into a 6 mol/L HCl solution. The adsorption isotherm of water and 2-propanol for the supports was determined at 298 K using a volumetric adsorption apparatus (Belsorp 18Plus-SP). Prior to the measurement the sample was degassed at 573 K for 3 h to remove physisorbed water.

2.4. Photoirradiation experiment

Photocatalytic properties of the composites, AS–CdS and Al_2O_3–CdS were evaluated with respect to hydrogen generation from water, as in the previous study [8], in the presence of 2-propanol as a sacrificial electron donor [11,12] for positive holes photogenerated on the CdS nanoparticles. About 0.02 g of sample of the composite was dispersed in 20 ml of a 10 vol% 2-propanol aqueous solution in a test tube. The mixture was purged with argon for 1 h, sealed with a septum, and then photoirradiated with a 2-kW xenon lamp (Ushio UXL-2003D-O). Irradiation light with wavelength $\lambda < 300$ nm and in the IR range was cut off by the Pyrex glass of the tube and by use of a water filter, respectively. The quantity of H_2 formed in the gas phase of the tube was measured by gas chromatography (Shimadzu GC-14B equipped with TCD), with a column packed with activated charcoal (2 m) and molecular sieve 5A (1 m) at a column temperature of 313 K.

3. Results and discussion

3.1. Immobilization of CdS nanoparticles on thiol-modified aluminosilicate supports

The absorption spectra for CdS nanoparticles in reverse micellar solution are shown in Fig. 1 for the case using Z331–SH as a typical example. The absorption corresponding to the CdS nanoparticles (curve (i)) disappears from the supernatant solution by the addition of Z331–SH (curve (ii)), whereas no change in the spectrum is observed in the case of the addition of Z331 particles without thiol modification