



Photocatalytic reactions of nanocomposite of ZnS nanoparticles and montmorillonite

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ABSTRACT

ZnS nanoparticles stabilized by cetyltrimethylammonium bromide (CTAB) were deposited on montmorillonite (MMT) forming a ZnS–CTA–MMT nanocomposite. The nanocomposite was characterized by scanning electron microscopy (SEM), Fourier transformed infrared (FTIR) and UV diffuse reflectance spectra (DRS) spectrometry, X-ray powder diffraction (XRD) and specific surface area measurements. Thereafter, it was used for photocatalytic reactions under UV irradiation (Hg lamp) in three different reaction media with different pH: NaOH solution, HCl solution and water. Prior to the photocatalytic reactions the dispersions were saturated by carbon dioxide to buffer the systems. The main reaction products in gas phase determined by gas chromatography were hydrogen and methane. The reactions were monitored by measuring oxidation–reduction potentials. The highest yields of hydrogen were obtained in the dispersion acidified by HCl but the concentrations of methane were similar in all tested media. Hydrogen was supposed to be formed by the reaction of two hydrogen radicals. Methane was formed by the reduction of carbon dioxide and by the partial decomposition of CTAB.

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1. Introduction

After the success of Fujishima and Honda in 1972 [1], when they photocatalytically split water into hydrogen and oxygen using a single-crystal TiO₂, many research papers devoted to heterogeneous photocatalysis have been published. There are several comprehensive overviews that summarize principles and applications of semiconductor photocatalysis (e.g. [2–6]). Generally, if semiconductors absorb a quantum of light ($h\nu$) electrons are excited to the conduction band and holes remain in the valence band. Some electrons and holes interact with each other (recombination) and some of them migrate to the semiconductor surface where they react with adsorbed compounds. Their reaction mechanisms are described in details by, e.g. Ohtani [6].

In our previous papers we investigated preparation of ZnS nanoparticles stabilized by a cationic surfactant CTAB and montmorillonite used as an inorganic support [7–10]. Montmorillonite and the ZnS nanoparticles formed a ZnS–CTA–MMT nanocomposite that exhibited photocatalytic activity for CO₂ reduction [7] and decomposition of phenol [10].

In this paper we aimed to compare the influence of different reaction mixtures on yields of the CO₂ photocatalytic reduction. Three aqueous media with different pH were compared: 0.2 mol L⁻¹

sodium hydroxide with initial pH of 12.2; distilled water with initial pH of 6.7 and 0.001 mol L⁻¹ hydrochloric acid with initial pH of 4.3. The photocatalytic experiments were performed with the nanocomposite of ZnS nanoparticles and montmorillonite [7,8].

2. Experimental

2.1. Preparation and characterization of ZnS nanocomposite

The ZnS nanoparticles were precipitated by zinc acetate and Na₂S in the presence of a stabilizing cationic surfactant cetyltrimethylammonium bromide [7,8]. The nanocomposite of these ZnS nanoparticles and montmorillonite was prepared by adding montmorillonite into the ZnS nanodispersion and shaking for 24 h. The solid part was filtered out and dried at 105 °C and stored for photocatalytic experiments.

The UV diffuse reflectance spectra of granulated ZnS–CTA–MMT (diameter of 0.25–0.50 mm) were recorded using a GBC CINTRA 303 spectrometer equipped with a spectralon-coated integrating sphere against a spectralon reference. The Kubelka–Munk function was calculated from the reflectance using the following formula: $F(R) = (1 - R)^2 / 2R$, where $F(R)$ is the Kubelka–Munk function and R is the reflectance.

Scanning electron microscopy was performed with an XL 30 Philips SEM instrument (Netherlands) equipped with a Robinson backscattered electron detector, which was used for examination

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of the nanocomposite morphology and zinc and sulphur distribution on the montmorillonite surface. The powdered samples were coated with gold and palladium in an ionization chamber before the examination. The elemental analysis of ZnS-CTA-MMT was performed by an EDAX detector.

FTIR spectra were obtained by the KBr (Mid IR) and polyethylene (Far IR) tablet methods using a Nicolet NEXUS 470 Fourier transform spectrometer (ThermoNicolet, USA). For each spectrum, 64 scans were obtained with a resolution of 8 cm^{-1} . The recorded FTIR spectra were normalized for the same weight of MMT and processed by means of the program OMNIC 7.3.

Specific surface area of MMT and the nanocomposite was measured with an instrument Sorptomatic 1990 (Thermo Electron Corporation, USA) using nitrogen as an adsorbing gas and calculated by the Advance Data Processing software according to the BET isotherm at a temperature of 77.3 K and p/p^0 ratio of up to 0.3.

2.2. Photocatalytic reactivity experiments

The photocatalytic reactions were carried out in a stirred batch annular reactor equipped with an on-line glass electrode for monitoring of pH, temperature and pressure. 0.1 g of the ZnS-CTA-MMT photocatalyst was suspended in 100 mL of the reaction medium and poured into the reactor. The volume of gas phase above liquid phase was 280 mL. Afterward the dispersion was saturated by pure carbon dioxide for 30 min until a constant pH was reached. The reaction was started by switching on the 8 W Hg UV lamp (254 nm). The temperature and pressure in the reactor were rapidly equilibrated at $30\text{ }^\circ\text{C}$ and 110 kPa, respectively.

Gas products were analyzed by a gas chromatograph equipped with flame ionization and thermal conductivity detectors. The relative standard deviation (RSD) of the CH_4 analysis was better than 10%, while RSD of the H_2 analysis was about 20%. The details of photocatalytic experiments and analytical methods were described in the previous work [11].

It is important to minimize the influence of transport phenomena during kinetic measurements. The elimination of CO_2 diffusion from the bulk of gas through the gas-liquid interface in the laboratory batch slurry reactor was accomplished by saturating the liquid phase with pure CO_2 before the reaction was started [12,13]. The suitable volume of liquid phase in our annular photoreactor to fulfil the requirement of perfect mixing was found at 100 mL [14].

3. Results and discussion

3.1. Preparation of ZnS nanocomposite

The ZnS nanoparticles were precipitated by mixing zinc acetate with sodium sulphide. The sulphide was added in excess (see Section 2) and thus sulphide ions were adsorbed on the nanoparticles surface according to the Paneth-Fajans rule causing their negative surface charge. The cationic surfactant CTAB was used to prevent their coagulation. The CTA cations were arranged around the nanoparticles forming positively charged ZnS-CTA micelles, which were created by ZnS cores and CTA bilayers formed on their surfaces. This was observed by measurements of their zeta-potential and sizes by the dynamic light scattering method and TEM and also confirmed by molecular modelling [9]. The mean size of the ZnS nanoparticles of about 5 nm was calculated from the band-gap energy of the ZnS-CTA dispersions and also evaluated from the TEM micrographs [9].

The resulting nanodispersion was then mixed with a clay mineral montmorillonite to immobilize the ZnS nanoparticles on a solid and inert carrier. As observed earlier, the ZnS nanoparticles

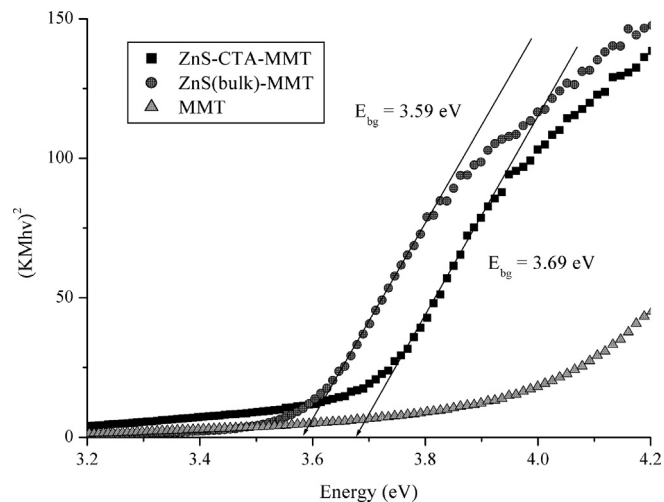


Fig. 1. DRS spectra of ZnS nanoparticles and bulk particles on montmorillonite.

filled MMT pores and after drying at $105\text{ }^\circ\text{C}$ they stayed enclosed inside them forming the nanocomposite ZnS-CTA-MMT [8].

3.2. Characterization of ZnS nanocomposite

The UV absorption spectra of the ZnS-CTA dispersions were shown in our previous paper [7,8]. They exhibited the absorption edge at 320 nm (3.88 eV). Here, the DRS spectra of the ZnS-CTA-MMT nanocomposite and bulk ZnS precipitated with no stabilization and deposited on MMT (ZnS(bulk)-MMT) were used to estimate the ZnS band-gap energies (Fig. 1).

As demonstrated in Fig. 1, the band-gap energies of the ZnS nanoparticles and bulk ZnS particles supported on MMT were 3.69 eV and 3.59 eV, respectively, which is lower than that of 3.70 eV corresponding to bulk ZnS. This effect of the MMT matrix is still unclear.

The SEM micrograph (Fig. 2a) demonstrates morphology of ZnS-CTA-MMT and location of ZnS nanoparticles on MMT. The SEM device equipped with the EDAX detector was able to map the location of zinc and sulphur on the ZnS-CTA-MMT surface. From Fig. 2a it is obvious that the ZnS nanoparticles were equally distributed over the examined surface. The EDAX analysis found the presence of zinc, sulphur and carbon confirming the presence of ZnS and CTA. Other elements were the components of montmorillonite.

The prepared nanocomposite was also characterized by FTIR spectrometry. Fig. 3 shows the IR spectra of ZnS-CTA-MMT and ZnS(bulk)-MMT. The stretching vibrations of C-H bonds at 2922 cm^{-1} (asym. $-\text{CH}_2-$) and 2851 cm^{-1} (sym. $-\text{CH}_2-$) confirmed the presence of CTA in the nanocomposite. The large bands at higher wavenumbers correspond to the stretching O-H vibrations in MMT octahedra (3629 cm^{-1}) and the stretching O-H vibrations of adsorbed water (3420 cm^{-1}). It can be seen that the content of adsorbed water in the nanocomposite was lower than that in ZnS(bulk)-MMT because CTA made the MMT surface hydrophobic. Strong stretching vibrations of Si-O bonds at 1045 cm^{-1} and bending vibrations at 520 cm^{-1} and 465 cm^{-1} corresponding to Al-O-Si and Si-O-Si bonds, respectively, were found as well. The absorption band at 1470 cm^{-1} corresponds to the C-N stretching vibration of CTA. The spectra in the far IR region (not shown here) were also recorded and weak vibration bands at 281 cm^{-1} of ZnS were identified.

X-Ray powder diffraction was used to recognize where the ZnS nanoparticles were located in the nanocomposite [7]. The MMT interlayer distance increased from 1.23 nm to 1.83 nm, which indicates that CTA was intercalated between the MMT layers. Therefore,

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