ZnS/MMT nanocomposites: The effect of ZnS loading in MMT on the photocatalytic reduction of carbon dioxide

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ABSTRACT

Different weight loadings (2–4.2 wt.%) of ZnS nanoparticles stabilized by cetyltrimethylammonium bromide (CTAB) were deposited on montmorillonite (MMT) in order to investigate the performance of ZnS/MMT nanocomposites in the CO_2 photocatalytic reduction. Physicochemical properties of prepared nanocomposites were comprehensively characterized by using nitrogen physisorption, XRD, TEM, DR UV–vis spectroscopy and contact potential difference measurements. The main reaction products in a gas phase were hydrogen and methane. According to the blank test the pristine montmorillonite did not possess any photocatalytic performance. The order in photocatalytic performance of individual ZnS/MMT nanocomposites in CO_2 reduction depending on the ZnS loading was following: 3.1 wt.% ZnS > 4.2 wt.% ZnS > 2.0 wt.% ZnS. This trend was explained based on UV–vis, TEM and contact potential difference measurements as follows. The increasing loading of ZnS nanoparticles affects the degree of ZnS nanoparticles agglomeration on MMT and this agglomeration finally influences the properties/behavior within electronic structure of ZnS, correlating with the photocatalytic performance of ZnS/MMT nanocomposites in the CO_2 reduction.

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1. Introduction

Carbon dioxide has increased in the atmosphere from fossil fuel use in industry and transportation, manufacture of cement, building air conditioning and deforestation. With a global radiative forcing of $1.74\,W/m^2$, CO_2 is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63% of the total [1]. Although the remediation of CO_2 can be physically stored or chemically transformed, its storage overcomes the problem only temporarily. To solve the CO_2 problem permanently requires the transformation of CO_2 into other valuable and non-toxic compounds. The reduction of CO_2 by photocatalysts is one of the most promising methods [1,2].

Several semiconductors exhibit band gap energies suitable for the photocatalytic reduction of carbon dioxide (for example CdS [3–7], ZrO_2 [8–13], MgO [14,15], ZnO [16], TiO_2 [17–27] and ZnS [2–6,28,29]). Zinc sulphide is a semiconductor with wide direct band gap energy of about 3.6 eV. It seems to be a very promising material for photocatalysis due to the rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of excited electrons.

In principle, inorganic materials with high specific surface area and chemical stability can be used as a host matrix, e.g. SiO_2, TiO_2, montmorillonite (MMT). Natural porous materials such as zeolites and clay minerals belong among good and cheap supports, moreover, with eco-friendly properties. Montmorillonite, a representative natural clay mineral, possesses a layered structure: two silica tetrahedral sheets and an alumina octahedral sheet. The adsorptive property is an advantage to enforce heterogeneous photoactivity when a semiconductor is immobilized [30–40].

Kun et al. [40] observed an increase of photoactivity in the photooxidation of phenol after deposition of TiO_2 in montmorillonite support. Results of these investigations showed that the porous structure and high specific surface area of montmorillonite were beneficial for photoactivity, via enhancing adsorption, which is the determining step in the heterogeneous photocatalytic reaction.

Therefore, the combining of adsorption and heterogeneous photocatalysis makes the photooxidation more effective for the removal of dye compounds from wastewater [30,32].

The effect of different $TiCl_3$:montmorillonite ratios on the photocatalytic activity in degradation of methylene blue in an aqueous solution was investigated by Liu et al. [36]. The nanocomposite with TiO_2:montmorillonite weight ratio of 0.2:1 showed the highest photocatalytic activity because of its relatively large specific surface area and suitable pore-size distribution.

Zhao et al. [37] dealt with the photocatalytic remediation of γ-hexachlorocyclohexane contaminated soils by using the TiO_2/montmorillonite composite. Their results indicated that the photocatalytic activity of the composites varied with the content of TiO_2 in the order 30% > 50% > 70% > 10% and the strong adsorption capacity of composites and the quantum size effect may contribute to increased photocatalytic activities.

The sulforhodamine B photodegradation over vanadium-doped TiO_2/montmorillonite nanocomposites was investigated under visible light irradiation [35]. It was revealed that different Ti/MMT ratios affect significantly the microstructure of nanocomposites and as a consequence their photocatalytic activity.

Tahir et al. [34] studied the performance of MMT-loaded TiO_2 nanocomposites in the reduction of CO_2 with H_2O to hydrocarbon fuels. The effect of parameters such as the MMT loading, H_2O/CO_2 feed ratios, and the reaction temperature on the TiO_2 photocatalytic activity was investigated. The MMT loading in TiO_2 enhanced the its performance and markedly increased the CO_2 reduction to C_1–C_3 hydrocarbon fuels.

Results from Boukhatem et al. [39], who dealt with the synthesis and characterization of CdS–montmorillonite nanocomposites and investigated their photocatalytic activity, showed that the photocatalytic activity of synthesized CdS/MMT nanocomposites was significantly improved compared to that of MMT and pure CdS.

Fatimah et al. [31] investigated the photocatalytic and photochemical degradation of methylene blue over ZnO/montmorillonite. Characterizations showed that the ZnO particles were successfully distributed in the montmorillonite support and ZnO/montmorillonite possesses lower band gap energy. The increased MB adsorption over ZnO/montmorillonite resulted in faster photodegradation.

The aim of this work is to explore the CO_2 photocatalytic reduction process on ZnS/MMT nanocomposites with 2.0, 3.1 and 4.2 wt.% of ZnS and to compare it with commercial TiO_2 Evonic P25. The effect of different ZnS to MMT weight ratios on the CO_2 photocatalytic reduction has not been reported yet. Likewise, the work function of ZnS/MMT nanocomposites has not been investigated. The aim is to reveal the correlations between structural, optical and electronic properties of developed nanocomposites and their photocatalytic performance. The photocatalytic reduction of CO_2 in our experimental arrangement takes place in liquid phase with suspended catalysts at room temperature and atmospheric pressure and the reduction products in gas phase are determined.

2. Experimental

2.1. ZnS/MMT nanocomposites preparation

Two-step preparation of ZnS/MMT was described in detail in our previous work [28]. Briefly, ZnS nanoparticles were formed by adding of the sodium sulphide and cetyltrimethylammonium bromide (CTAB) solution (solution A) dropwise to the solution of zinc acetate (solution B). The ZnS-CTAB was subsequently deposited on montmorillonite by shaking 1 L of 2 mM ZnS solution with 2 g of MMT for 24 h followed by filtration, washing and drying. Two variations in the above-described synthesis were done in order

to positively influence the resulting nanocomposite efficiency. The first one, the addition of the solution B to the solution A changes pH during the ZnS nanoparticles nucleation since sodium sulphide is a base. The composite obtained by shaking such formed ZnS nanoparticles with MMT was denoted as 4.2 wt.% ZnS/MMT. The second variation, the ratio of ZnS suspension volume to MMT weight was varied from 1:2 (L:g) to 1:4 and 1:8, resulting in nanocomposites denoted as 3.1 wt.% ZnS/MMT and 2.0 wt.% ZnS/MMT.

2.2. Characterization of ZnS/MMT nanocomposites

The content of ZnS in ZnS/MMT nanocomposites was determined by elemental analysis of sulphur performed by a combustion analyser ELTRA (Eltra, Germany) and determination of zinc after their dissolution in a mixture of HF, HNO_3 and $HClO_4$ [41] by an atomic absorption spectrometer AA280FS (Varian Inc., Austria).

The nitrogen adsorption–desorption measurements at 77 K were performed using the volumetric apparatus Nova2000e (Quntachrome, USA). Prior to the nitrogen physisorption measurements, the samples were degassed at 105 °C for 4 h under vacuum less than 1 Pa. Degassing at temperature of 105 °C was applied in order to remove physisorbed water, however, with no influence on the textural or structural properties of investigated nanocomposites. The specific surface area, S_{BET}, was calculated according to the classical Brunauer–Emmett–Teller (BET) theory for the relative pressure range p/p_0 = 0.05–0.30 [42]. Since the specific surface area, S_{BET}, is not such a proper parameter in the case of mesoporous solids containing some micropores [42,43], the mesopore surface area, S_{meso}, and the micropore volume, V_{micro}, were additionally also evaluated based on the t-plot method [44], using DeBoer standard isotherm. The net pore volume, V_{net}, was determined from the nitrogen adsorption isotherm at maximum p/p_0 (~0.991). The mesopore-size distribution (pore diameter 3–130 nm) was evaluated from the adsorption branch of the nitrogen adsorption–desorption isotherm by the Barrett–Joyner–Halenda (BJH) method [45], using the DeBoer standard isotherm and the assumption of the cylindrical pore geometry.

The X-ray diffraction powder (XRD) patterns were measured by a standard laboratory diffractometer in the conventional focusing Bragg-Brentano geometry with variable slits (Ni-filtered Cu Kα, 1.4 kW). A linear detector was used to collect the scattered intensity.

Transmission electron microscopy (TEM) observations were carried out on a JEOL 2010F microscope operated at 200 kV (LaB6 cathode, resolution 0.19 nm) using carbon coated copper grid.

UV–vis diffuse reflectance spectra of prepared samples (grain size < 0.160 mm) were measured by using a GBS CINTRA 303 spectrometer equipped with a Spectralon-coated integrating sphere using a Spectralon coated discs as a standard. The spectra were recorded in the range of the wavelength 200–800 nm (lamps switched at 350 nm). The reflectances were re-calculated to the absorption using the Schuster–Kubelka–Munk equation, $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. The obtained spectra were transformed to the dependencies $(F(R_\infty) \cdot h\nu)^2$ against $h\nu$ and assuming that the Tauc's law [46,47] can be expressed as: $(F(R_\infty) \cdot h\nu)^2 \approx (h\nu - Eg)$, where the Eg is the energy of absorption edge values (determined from obtained plots), h is the Planck constant and ν is the light frequency. Kubelka–Munk function was used to estimate the band gap energy of prepared photocatalysts. The optical absorption threshold (lg) was calculated using the equation, lg = 1240/EB, where EB is the band gap energy.

The contact potential difference (V_{CPD}) measurements were carried out by the dynamic condenser method of Kelvin with a KP6500 probe (McAllister Technical Services). The reference electrode was a standard stainless steel plate with diameter of 3 mm (Φ_{ref} = 4.3 eV)