

Proc. of the International Conference on Mechanochemistry and Mechanical Alloying, Kraków, Poland, June 22–26, 2014

Photocatalytic Properties of Mechanochemically Synthesized Nanocrystalline ZnAl_2O_4 and CdSe

N.G. KOSTOVA^{a,*}, AL. ELIYAS^a, M. FABIÁN^b, M. ACHIMOVIČOVÁ^b AND P. BALÁŽ^b

^aInstitute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

^bInstitute of Geotechnics, Slovak Academy of Sciences, Košice, Slovakia

Nanocrystalline powders of ZnAl_2O_4 and CdSe were prepared via mechanochemical synthesis. Powder slurries were coated as thin films on SiO_2 thin layer chromatography (TLC) sheet by capillary method. The photocatalytic activity of the film coating was tested in a self-made gas-phase flat-plate continuous-flow photocatalytic reactor with toluene as model air contaminant. The tested nanocrystalline ZnAl_2O_4 turned out to be poor oxidation photocatalyst under UV irradiation. CdSe displays considerable photocatalytic activity under visible light, where TiO_2 is inactive. The nonconventional one-step mechanochemical route to ZnAl_2O_4 and CdSe synthesis offers several advantages compared to traditional processing routes, including low-temperature solid state reactions at ambient temperature, absence of organic templates contamination and low expenses.

DOI: [10.12693/APhysPolA.126.967](https://doi.org/10.12693/APhysPolA.126.967)

PACS: 81.20.-n, 61.05.cp, 61.46.-w, 61.66.Fn

1. Introduction

The environmental pollution is a major problem in contemporary society. The BTX aromatics (benzene, toluene, xylenes) are prevailing volatile organic compounds (VOC) in closed premises. These are toxic inflicting serious health problems for the population. Heterogeneous photocatalysis over semiconductors is a promising method, applied successfully for the destruction of organic contaminants, combining the advantages of low expenses and mild reaction conditions. We chose ZnAl_2O_4 and CdSe as representatives of two different types of semiconductors. Zinc aluminate spinel (ZnAl_2O_4) has attracted recently some attention as a catalyst due to its high thermal stability, high mechanical strength, and low surface acidity. Several methods have been known so far for its synthesis in the form of nanoparticles: sol-gel [1], microwave-hydrothermal [2], and solvothermal method [3]. CdSe is an important II-VI type of semiconductor with bulk phase band gap energy of 1.75 eV [4, 5] utilizing lower energy photons, compared to TiO_2 . CdSe nanocrystals are prepared by chemical wet process mainly [6]. Mechanochemical synthesis in planetary ball mill produces surface clean semiconductor nanoparticles without the influence of organic ligands [7]. The purpose of this paper was to study the mechanochemically synthesized ZnAl_2O_4 and CdSe as photocatalysts for toluene degradation.

2. Experimental

The mechanochemical route was used for the preparation of nanocrystalline zinc aluminate. A mixture of γ -

Al_2O_3 and ZnO (99.9% purity) reactants at a molar ratio of 1:1 was milled continuously for various time intervals in Pulverisette 7 planetary ball mill (Fritsch, Germany) at room temperature and 550 rpm. A grinding chamber and balls made of tungsten carbide were used. The ratio between the weight of grinding ball and that of the powder was 40:1. The XRD patterns of zinc aluminate samples were collected using a Phillips PW 1820 (Netherlands) diffractometer with $\text{Cu } K_\alpha$ radiation.

Mechanochemical synthesis of cadmium selenide was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany) by milling of cadmium powder (99%, Aldrich, Germany) and selenium powder (99.5%, Aldrich, Germany) at a molar ratio 1:1 in argon atmosphere. The following experimental conditions were used for the mechanochemical synthesis: loading of the mill, 50 balls of 10 mm in diameter; material of milling chamber and balls, tungsten carbide; volume of milling chamber, 250 mL; ball-to-powder ratio 73:1; room temperature; rotational speed of the mill planet carrier, 500 rpm; milling time, 30 min. X-ray diffraction measurements of cadmium selenide sample was carried out using a D8 Advance diffractometer (Bruker, Germany) equipped with a θ/θ goniometer, $\text{Cu } K_\alpha$ radiation (40 kV, 40 mA), a secondary graphite monochromator, and a scintillation detector. The diffraction data were collected over an angular range $20 < 2\theta < 70^\circ$ with steps 0.03° and a counting time of 5 s/step. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

The specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

The testing of the photocatalytic activity of a powder sample of semiconductors was carried out in a gas-phase flat-plate flow-circulation photocatalytic reactor with toluene as a model contaminant of the air. The flow-

*corresponding author; e-mail: nkostova@ic.bas.bg

circulation mode was applied by connecting the reaction and a gas-circulation pump in a contour having circulation rate more than 50 times higher than the inlet flow rate of the gaseous mixture. This system ensures ideal mixing type of reactor, which operates in the kinetic region. This flow-circulation reactor configuration is superior to the continuous flow reactor configuration (plug-flow type of reactor), where the photocatalytic reaction occurs in the diffusion region with some diffusion retardation effects lowering the conversion degree of the model contaminant under the same remaining reaction conditions (humidity, type of illumination, intensity of illumination, distance of illumination). The course of the photocatalytic reaction of complete oxidation of toluene was monitored by a gas-analyzer (LANCOM III, Land Instruments Co., England) equipped with chemisorption sensors. The inlet gas mixture was fed to the reactor through three channels of an electronic mass flow regulator (Matheson model 8249).

Two channels were used for feeding the nitrogen — the first one fed the N₂ flow over a graduated sealed-bottom capillary toluene saturator of 1 ml volume. The second nitrogen flow passed through a saturator with distilled water (moist N₂) and then into the reactor, ensuring complete saturation of the feed gas mixture with water vapor at the given temperature and flow rate, as the powder metallurgy frit gave very tiny bubbles of N₂ through the water layer. The use of two independently regulated channels for feeding N₂ enabled the variation of the humidity of the gaseous mixture. This is a very important operational parameter in photocatalysis as the water vapor is the source of hydroxyl radicals under UV-light irradiation (the main active species, oxidizing non-selectively all classes of organic compounds). Our previous experiments with TiO₂ Degussa P25 established that the optimal relative humidity (RH) was about 30% and it has been calculated in the following way:

$$\text{RH} = \left[\frac{F_{\text{N}_2\text{moist}}}{(F_{\text{N}_2\text{toluene}} + F_{\text{N}_2\text{moist}} + F_{\text{O}_2})} \right] \cdot 100\%, \quad (1)$$

where F_i denote the respective flow rates of the feed gases (ml/min).

The course of the photocatalytic reaction to complete oxidation of toluene was monitored by gas-analyzer equipped with chemisorptions sensors. The LANCOM gas analyzer enabled monitoring both the partial oxidation (by means of the CO sensor), the complete oxidation (by means of the CO₂ sensor), the concentration of the unreacted C₆H₅CH₃ at the reactor outlet (by means of the C_xH_y sensor) and that of O₂, allowing material balance and evaluating experimental error.

2.1. Types of illumination and intensity of illumination

2.1.1. UV-A light

The width of the flat-plate quartz glass illumination window (dimensions 5 cm × 15 cm × 0.5 cm) of the reactor enabled simultaneous accommodation of two 4 W lamps (Philips TL4W/08 F4T5/ BLB) of total power

8 W, placed directly upon the window (0 cm illumination distance, intensity of illumination 0.014 W/cm²) — polychromatic light with wavelengths 320–400 nm.

2.1.2. UV-C light

Two lamps TUV 4W/G4 T5 (monochromatic light $\lambda = 254$ nm) of 4 W (a total of 8 W), located on the illumination window (0 cm illumination distance, intensity of illumination 0.014 W/cm²) but the photons have higher energy.

2.1.3. Visible light

The visible light irradiation was accomplished by means of a linear halogen lamp Tunggram 500 W. K1R7s afforded illumination intensity of 8.9 mW/cm² (9700 Lm) at 50 cm illumination distance. The remaining operational conditions — flow rate and humidity were the same as those with the UV light. The POLITEF photocatalytic reactor enabled the option to use visible light irradiation, as material POLITEF (teflon) was stable at elevated temperatures (up to 260 °C).

2.2. Testing of the photocatalytic activity

The results from the steady-state measurements of the photocatalytic activity under illumination with different kinds of light are summarized in Table. All the data refer to optimal relative humidity (30% RH) and large excess of oxygen in the feed mixture at the reactor inlet. The degree of conversion of toluene was a measure of the photocatalytic activity. The inlet concentration of toluene was 1000 ppm C_xH_y (LANCOM gas analyzer). Taking into account the band gaps of the photocatalytic materials — the following types of illumination were applicable CdSe band gap of 1.75 eV (UV-C, UV-A, visible light absorption), Degussa P25 reference photocatalytic material (TiO₂ anatase band gap of 3.2 eV, TiO₂ rutile band gap of 3.0 eV — both UV and visible light could be applied) and 3.8 eV for the ZnAl₂O₄, which implies using only UV-C light with sufficiently high photon energy.

TABLE

Comparison of the degrees of photocatalytic conversion of toluene under different illuminations, 30% RH and O₂ excess over CdSe and ZnAl₂O₄ photocatalysts with the data for TiO₂ photocatalyst Degussa P 25 (coating 1 mg/cm²). #1 — photocatalyst film, #2 — conversion C₆H₅CH₃ [%], #3 — type of illumination, #4 — illumination intensity [W/cm²], #5 — distance of illumination [cm]

#1	#2	#3	#4	#5
CdSe	2.5	UV-A	0.014	0
CdSe	4.3	UV-C	0.014	0
CdSe	11.6	Visible	8.9	50
TiO ₂ Degussa P25	12.8	UV-A	0.014	0
TiO ₂ Degussa P25	27.3	UV-C	0.014	0
TiO ₂ Degussa P25	0	visible	8.9	50
ZnAl ₂ O ₄	1.9	UV-C	0.014	0

3. Results and discussion

The milling of the mixture of alumina and ZnO led to phase transformation. The XRD pattern of initial mixture (Fig. 1) is characterized by sharp diffraction peaks corresponding to crystalline ZnO (JCPDS PDF 36-1451). The γ -Al₂O₃ prepared by decomposition of Al(OH)₃ at 600 °C has lower degree of crystallinity than that of ZnO and for this reason the peaks corresponding to γ -Al₂O₃ are not visible in the common XRD pattern before the high energy ball milling (Fig. 1). After 6 h of milling, the powder was transformed into the ZnAl₂O₄ phase (JCPDS PDF 05-0669) (Fig. 1). Nanocrystalline zinc aluminate was the product of the mechanochemical reaction.

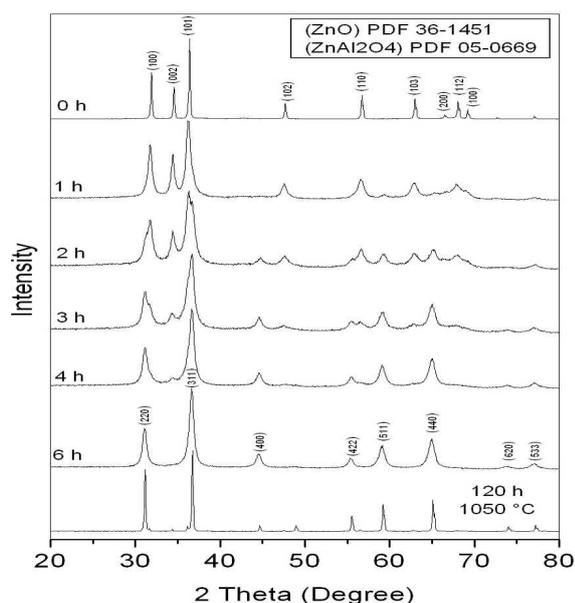


Fig. 1. XRD patterns of mechanochemically prepared ZnAl₂O₄.

The X-ray diffraction pattern of mechanochemically synthesized CdSe is shown in Fig. 2. The XRD peaks were identified based on the JCPDS card 19-191 and corresponded to cubic cadmium selenide — CdSe phase. The large broadening of X-ray diffraction reflections also confirmed the nanocrystalline nature of the cadmium selenide prepared by mechanochemical synthesis. The value of specific surface area, S_A of mechanochemically synthesized CdSe is also displayed in Fig. 2.

The value of specific surface area, S_A , of mechanochemically synthesized CdSe was 4 m²/g. The nanosized mechanochemically synthesized ZnAl₂O₄ possessed S_A equal to 38 m²/g, which is lower than that of P25 Degussa (50 m²/g).

3.1. Deposition of a thin film of photocatalyst on a TLC sheet

The support bearing the CdSe or ZnAl₂O₄ photocatalytic layer (previously TiO₂) was a commercially

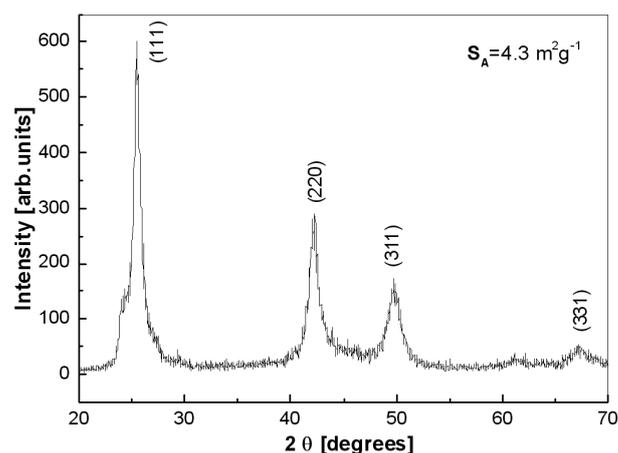


Fig. 2. X-ray diffraction pattern of CdSe mechanochemically synthesized for 30 min.

available Al foil, covered with silica gel (0.2 mm TLC Merck Art.5554 Kieselgel 60 F₂₅₄). A rectangular piece (4.2 cm × 13.4 cm) was easily cut out of the plate (25 cm × 25 cm) and placed in the nest of the reactor (total geometric area 56 cm²). An amount of 56 mg of the powder sample CdSe (ZnAl₂O₄) was weighed (to obtain a coating of 1 mg CdSe/cm² or ZnAl₂O₄) and suspended in de-ionized water. The suspension (56 mg CdSe/ZnAl₂O₄ in 5 ml H₂O) was sonicated for 30 min using an ultrasonic processor Hielscher UP 200S (Germany, 24 kHz) to disperse effectively the CdSe agglomerates. Then the finely dispersed suspension was deposited by the capillary method by directing air stream uniformly all over the TLC sheet and was dried until constant weight is obtained. Then the photocatalytic coating is mounted in the reactor and tested.

The data in Table show that the activity of the CdSe semiconductor photocatalyst under UV irradiation is much lower, compared to the reference photocatalyst (TiO₂ Degussa P25), meaning lower photonic efficiency of the CdSe material, compared to that of TiO₂. In both cases the UV-C irradiation was more effective than the UV-A illumination, giving higher toluene conversion at one and the same illumination of 0.014 W/cm². However, in case of visible light illumination the CdSe material is superior to the TiO₂ photocatalyst (zero photocatalytic activity under visible light irradiation of the latter). ZnAl₂O₄ displays very low photocatalytic activity and only under UV-C light. Altogether the activities in toluene photooxidation are twice lower than those in the case of ethylene degradation (15.2% with UV-A and 40.1% with UV-C) at ten times lower model contaminant concentrations (1000 ppm for toluene in comparison to 10 000 ppm for ethylene), although in the case of toluene kinetic region of operation was achieved by flow-circulation (ethylene experiments were diffusion controlled in continuous flow mode). This is due to the stability of the benzene ring in the toluene molecule.

4. Conclusions

The CdSe semiconductor is a promising photocatalyst for air decontamination in view of its activity under visible light. In this case the traditional disadvantage of CdSe in aqueous phase (when applied for waste water decontamination it is unstable and quickly hydrolyses) has been overcome by depositing CdSe on immobilized fixed support. At moderate relative humidity of the contaminated air stream of about 30% the supported thin film of CdSe is stable and it is operable for long periods of time. The CdSe photocatalyst has much lower activity for oxidative removal of toluene in air compared to the traditional TiO₂ photocatalyst Degussa P25 under UV-light irradiation. However CdSe displays considerable photoactivity with visible light, where TiO₂ is inactive. The ZnAl₂O₄ semiconductor material has poor photocatalytic activity, which is manifested only with UV-C light. The toluene molecule is much more stable to photocatalytic oxidative degradation in comparison to the ethylene and it is recommendable to use much lower feed concentrations of toluene at the inlet of the photocatalytic reactor and to carry out all the experimentation in the kinetic regime, ensured by the flow-circulation system.

Acknowledgments

The authors acknowledge gratefully the financial support through the National Science Fund (Bulgaria) with the projects DNTS/Slovakia 01/3 and DFNI E 01/7/2012 and Agency for Science and Development (Slovakia) with the projects APVV-Sk-Bg-0031-10 and APVV-0189-10.

References

- [1] R.K. Sharma, R. Ghose, *Ceram. Int.* **40**, 3214 (2014).
- [2] M. Zawadzki, *Solid State Sci.* **8**, 14 (2006).
- [3] W. Staszak, M. Zawadzki, J. Okal, *J. Alloys Comp.* **492**, 500 (2010).
- [4] G. Han, L. Wang, C. Pei, R. Shi, B. Liu, H. Zhao, H. Yang, S. Liu, *J. Alloys Comp.* **610** 62 (2014).
- [5] P. Wang, D. Li, J. Chen, X. Zhang, J. Xian, X. Yang, X. Zheng, X. Li, Y. Shao, *Appl. Catal. B Environm.* **160-161**, 217 (2014).
- [6] G.G. Yordanov, H. Yoshimura, C.D. Dushkin, *Colloid Surf. A Phys. Chem. Eng. Asp.* **322**, 177 (2008).
- [7] P. Balaz, *Mechanochemistry in Nanoscience and Mineral Engineering*, Springer, Berlin 2008.