



Structural evolution in Pt/Ga-Zn-oxynitride catalysts for photocatalytic reforming of methanol



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ABSTRACT

Products of microwave-assisted urea-induced co-precipitation of $\text{Ga}(\text{NO}_3)_3$ and $\text{Zn}(\text{NO}_3)_2$ or Ga_2O_3 and ZnO were nitridated in order to obtain Ga-Zn-based photocatalysts. Irrespectively to the starting material, wurtzite-like Ga-Zn-oxynitride phases formed. The preparation was completed by deposition of a Pt co-catalyst, which was activated by either reduction in hydrogen or calcination in air. It was demonstrated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) that during oxidative activation the oxynitride started to transform into a nitrogen-free Zn-containing Ga- oxyhydroxide. Regardless to the structure of the catalysts after the activation step, almost complete oxynitride to oxyhydroxide transformation was observed during the methanol photocatalytic reforming reaction, accompanied by complete reduction of the Pt co-catalyst to metallic state. The observations of this study point to the importance of phase transitions under reaction conditions in the development of the active ensemble in the Ga,Zn-based photocatalysts.

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1. Introduction

Photocatalytic hydrogen production is a promising approach for storing solar energy in chemical form. High gravimetric energy density, abundance and storage potential make hydrogen a potential energy carrier [1]. It has great promise for utilizing in clean, high-efficiency power generation systems such as fuel cells.

Methanol is a good hydrogen resource because of its high hydrogen/carbon ratio. Significant efforts have been made for photo-induced reforming of methanol. The idea is to use an efficient photocatalyst together with solar energy to promote H_2 formation from methanol according to Eq. (1) [2]:



Ga-oxynitride [3–5] and Ga-Zn-oxynitride [4] photocatalysts can be efficiently applied for utilizing visible light [6], they are good candidates for photocatalytic reforming of methanol [5,7]. Both materials are semiconductors, their band gaps are reduced [5] in comparison to GaN (~3.4 eV), ZnO (~3.2 eV) and Ga_2O_3 (~4.6 eV). Ga-oxynitrides have a chemical formula of $(\text{Ga}_{1-x}\square_x)(\text{N},\text{O})$ and can

adopt the wurtzite-type structure of the hexagonal GaN (GaN_h), in which O substitutes for N and the octahedral sites are randomly occupied by Ga and vacancies [3]. In Refs. [8–10] a range of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ materials were synthesized; these wurtzite-type phases can be regarded as solid solutions of the two constituents GaN and ZnO, in which Ga and Zn randomly occupy the octahedral cation sites. The Ga-Zn-oxynitride $((\text{Ga}_{1-x}\text{Zn}_x)(\text{N},\text{O}))$ structure can be related to the GaN-ZnO solid solution structure by incorporation of more O to the N sites and compensating vacancies to the cationic sites, resulting in an imperfect wurtzite-type material.

Ga-oxynitrides, Ga-Zn-oxynitrides and GaN-ZnO solid solutions, which are isostructural with GaN_h , are commonly synthesized via high temperature ammonolysis of the appropriate oxide [8–10] or hydroxide precursors [4,5]. However, many parameters of the preparations, among others temperature and duration of the ammonolysis, geometry of the reactor, the gas flow and even the pre-calcination of the precursor ZnO [8], can significantly influence the properties, thus the activity of the photocatalysts. In particular, the degree of the crystallinity in Ga-Zn-oxynitrides increases with increasing nitridation time and in parallel the Zn and O concentration decreases because the significant part of the ZnO precursor is removed as a result of reduction and volatilization of the Zn [9]. The decrease of nitridation temperature, as a method of

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controlling ZnO concentration, results in Ga-Zn-oxynitrides with poor crystallinity, phase separation and mixed surface oxide formation leading to poor photocatalytic activity [11]. Literature data suggests that Ga(OH)₃ behaves as a more suitable precursor for Ga-oxynitride synthesis than Ga₂O₃ because its crystal lattice contains unoccupied 12-coordinate sites, which facilitate the ionic transport during the nitridation [5]. The abundance of vacancies at the octahedral sites in Ga-oxynitrides can be reduced by increasing the nitridation temperatures in the range of 750–850 °C [3] and the vacancies can be eliminated by introducing Zn²⁺ into the structure, during which a complete solid solution of (Ga_{1-x}Zn_x)(N_{1-x}O_x) forms [4].

The photocatalytic activity of the semiconductors can be significantly improved by applying co-catalysts [12–15]. The H₂ formation in the methanol photocatalytic reforming reaction increases several orders of magnitude if co-catalysts have been introduced onto the surface of the semiconductor [16–18]. In the absence of co-catalysts, semiconductors induce poor H₂ evolution even in the presence of any sacrificial electron donor [13]. Co-catalysts promote the charge separation and suppress the recombination of the photogenerated electron-hole pair [13,14]. Another less emphasized but important role of the co-catalyst is to provide reaction sites for elementary reaction steps subsequent to light absorption, such as formation of molecular hydrogen and its desorption from the surface. If the surface reaction is too slow to consume the charges, the probability of charge recombination increases [13].

Noble metals such as Ag, Au, Pt and oxides such as RuO, NiO_x are considered to be effective co-catalyst. Regarding the photocatalytic hydrogen production, Pt with the largest work function is not only the best co-catalyst for electron trapping but it shows excellent catalytic activity for H⁺ reduction and promotes the combination of surface hydrogen atoms into molecular H₂ as well [13]. According to literature data, Pt has the lowest activation energy for H₂ evolution [19]. In addition, Pt not only drains electrons from the semiconductor but transfers them to the solution, while other metals such as Au, Ag and Cu store the excess electrons on the metal surface due to the Helmholtz capacitance of the metal-solution interface, rather than transport electrons directly to the solvent [20,21]. Consequently, Pt is considered as the most suitable hydrogen evolution co-catalyst because of its excellent electronic and catalytic properties [13].

In order to load co-catalysts on the surface of the semiconductors several methods are available. Commonly used techniques include *in situ* photodeposition [5,12,22] and deposition of pre-prepared metal colloids [23–26]. An easy and effective way for preparing co-catalysts is impregnation with the appropriate metal salt followed by calcination. A series of metal oxide co-catalysts (such as NiO_x, RuO₂, RhO_x, and PtO_x) can be built on the surface of Ga-Zn-oxynitrides by means of this method [27]. RuO₂ can also be loaded via impregnation by tetrahydrofuran solution of Ru₃(CO)₁₂ followed by drying and calcination [9]. Calcination of the Ga-Zn-oxynitride support itself is preferred because the treatment eliminates the traces of metallic Zn, which are potential recombination centers [28]. According to [29,30], the Rh_x-Cr_y-oxide pair, obtained by co-impregnation (co-evaporation) followed by calcination, is one of the most effective co-catalysts in the overall water splitting on Ga-Zn-oxynitrides. However, this co-catalysts/semiconductor system is less effective in the methanol photocatalytic reforming reaction [31]. High temperature reduction of the metal precursor [32] in H₂ is one of the most commonly used methods to prepare supported metal catalysts, but it is believed unsuitable for oxynitrides because of their limited thermal stability compared to oxides [33].

In this contribution the structural stability of the Ga-Zn-oxynitride/Pt co-catalyst system is discussed. The effect of the

synthesis steps on the structural properties of the catalysts is compared in case of two distinct Ga-Zn precursor compounds. The study is completed by exploring the structural evolution of the catalyst systems during the reaction conditions of photocatalytic H₂ production.

2. Materials and methods

2.1. Materials

Ga(NO₃)₃ (Aldrich), Ga₂O₃ (Aldrich), ZnO (Aldrich), GaN (Aldrich), Pt(NH₃)₄(NO₃)₂ (Aldrich), Zn(NO₃)₂ × 6H₂O (Fluka), urea (Molar Chemicals Ltd., Hungary) were used as received. Methanol and NH₄OH solution were purchased from Reanal (Hungary). Double distilled water (18 MΩ) was used in every experiments.

2.2. Synthesis of the photocatalysts

We assumed that homogeneous distribution of the components was favorable to retain Zn during the nitridation process. Therefore a co-precipitation method starting from Ga and Zn salts was chosen to obtain the precursors for high temperature NH₃ treatment. The Zn/Ga starting (Zn/Ga_{nom}) ratio was controlled by the amount of the precursor materials. For example, in order to achieve a Zn/Ga_{nom} atomic ratio of 0.32, we dissolved 2.43 g Ga(NO₃)₃ and 0.89 g Zn(NO₃)₂ × 6H₂O in 50 ml water and added 1.03 g urea. The mixture was irradiated in a microwave reactor for 30 min at 120 °C. Then the mixture was stirred at 60 °C as long as the NH₃ gas liberated (checked by the color change of the pH paper over the mixture). As a result a precipitate formed, which was separated by centrifugation and washed with 3 × 50 ml water to remove the nitrate. The sample was dried in an oven at 90 °C for overnight. The nitridation was carried out in a quartz reactor using 100 ml/min NH₃ flow at 800 °C for 10 h. The relatively low temperature was chosen in order to reduce the release of Zn. For comparison, the same preparation steps were performed by mixing Ga₂O₃ and ZnO starting materials with Zn/Ga_{nom} ratio of 0.32. We also synthesized samples with Zn/Ga_{nom} = 0.14 from both the nitrate and oxide starting materials. The quality and behavior of the prepared samples were compared to commercial GaN.

As a co-catalyst, 1% Pt was introduced by impregnation with the aqueous solution of Pt(NH₃)₄(NO₃)₂. After overnight drying at 90 °C, the samples were either calcined for 1 h at 300 °C in an oven using 1 °C/min heating rate or were reduced in 30 ml/min H₂ flow at 400 °C for 1 h using stepwise heating in H₂ after purge with N₂ at 150 °C for 15 min.

2.3. Characterization of the photocatalysts

X-ray powder diffraction (XRD) patterns were obtained in a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using CuKα radiation (λ = 0.15418 nm), graphite monochromator and proportional counter. Silicon powder (NIST SRM 640) or corundum were used as internal standards and the scans were evaluated with profile fitting methods. During phase analysis we used reference cards from the ICDD PDF-2 (1998) data base. The cell parameters of the crystalline phases were determined from the d-values of all the reflections. Crystallite sizes were calculated from reflection line broadening using the Scherrer-equation.

TEM studies of the samples were carried out in a FEI Morgagni 268D type transmission electron microscope (accelerating voltage: 100 kV, W-filament). The samples were prepared by grinding and dispersing of the resulted powder in ethanol using an ultrasonic bath. Energy Dispersive X-ray Spectrometry (EDX) analysis was performed by an INCA (Oxford Instruments Ltd.) detector and an

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