



Novel cerium doped titania catalysts for photocatalytic decomposition of ammonia



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ABSTRACT

Parent TiO₂ and cerium doped TiO₂ photocatalysts (with cerium loadings in the range 0.6–1.4 wt.%) were prepared by using the sol–gel method controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane. Textural, structural, microstructural, optical and electronic properties of photocatalysts were characterized in detail by using nitrogen physisorption, powder X-ray diffraction, diffuse reflectance UV–vis spectroscopy and contact potential difference measurements. It was proved that increasing amount of cerium ions in TiO₂ decreases the anatase crystallites size, which corresponded to the increase of specific surface area of the catalysts. The shift of spectral response of cerium doped catalysts to the visible light region was also observed, the significant decrease of absorption edge of photocatalysts with increasing Ce loading within 0.6–1.4 wt.% was detected. The photocatalytic decomposition of ammonia was carried out in a stirred batch annular reactor and the main product was hydrogen. The energetics of the TiO₂ photocatalysts, which were crucially affected by the doping with Ce ions, play the key role in the ammonia photocatalytic decomposition.

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1. Introduction

Ammonia is a common water contaminant with strong effects on environment and human health. The term ammonia includes nonionized form (NH₃) and the ammonium cation (NH₄⁺) unless stated otherwise. Ammonia is mostly used in fertilizers and animal feed production and in the manufacture of fibers, plastics, explosives, paper and rubber. It is an important pollutant containing nitrogen and source of nutrients that may accelerate the eutrophication and cause algal growth in natural water. Natural levels in groundwater and surface water are usually below 0.2 mg/l. The threshold odor concentration of ammonia in water is approximately 1.5 mg/l.

Disposal of ammonia contaminated waters, no matter what origin, is not a trivial. Several methods have been developed and

applied for the treatment of ammonia-containing wastewater, including biological processes, air stripping, ion exchange, breakpoint chlorination, and chemical oxidation [1,2]. Among these methods, biological processes are generally regarded to be the most efficient. However, these processes have disadvantages, including handling difficulties and large equipment requirements. Moreover, they are difficult to apply for the treatment of wastewater that contains for bacteria harmful co-existing species [3].

The photocatalytic reaction seems to be the right way for decreasing ammonia concentrations in waste water. The most of studies have concerned on ammonia photocatalytic oxidation to possible products such as N₂, N₂O, NO₂, NO₃⁻ over titanium dioxide [4–10], TiO₂ perlite [11], TiO₂/LECA (light expanded clay aggregate) [12,13], platinum loaded titanium dioxide [3,14–16], titanate nanotube [17,18], and Cu/TiO₂/SiO₂ modified with nitrogen [19].

On the contrary, only a few studies focused on the photocatalytic ammonia decomposition to nitrogen and hydrogen. Li et al. [20] investigated photodecomposition of ammonia over NiO and RuO₂ loaded SrTiO₃ and BaTiO₃. Nemoto et al. [21] reported about

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optimum platinum loading TiO₂ and reaction pH for the photocatalytic decomposition of ammonia in aqueous solution. Kominami et al. [22] studied NH₃ photocatalytic decomposition over metal-loaded TiO₂ (Pt, Pd, Au, Ag, Cu, Ir). The best catalyst for this reaction was platinum-loaded TiO₂. Yazawa et al. [23] investigated reaction mechanism of ammonia decomposition to nitrogen and hydrogen over metal loaded titanium dioxide photocatalyst. The photo-formed hole on the titanium oxide oxidizes NH₃ to form amide radical (*NH₂) and proton. The amide radicals produce hydrazine (N₂H₄), and it can be further decomposed to form nitrogen and hydrogen. They also investigated the addition of different metals – Pt, Rh, Pd, Au, Ni, Cu – to titanium dioxide and found out Pt/TiO₂ photocatalyst exhibited the best activity.

There is also another important advantage in the photocatalytic NH₃ decomposition. Ammonia is attracting great attention as a possible energy source due to production of hydrogen from its decomposition.

To best of our knowledge, cerium modified TiO₂ has never been tested for the photocatalytic decomposition of ammonia. We used cerium doped TiO₂ in our previous work [24] where the influence of different amount of cerium (0.6 wt.%–21.1 wt.%) on the yields of the photocatalytic reduction of carbon dioxide was tested. Based on experimental data, it was found out that the addition of cerium lowers the band gap of the photocatalyst. The most efficient catalyst was the one with the lowest amount of cerium (0.6 wt.%). In this case the band gap was lowered and also the excited electrons had potential high enough to reduce H⁺/H₂. Therefore, the series of cerium doped TiO₂ with lower amounts of cerium (0.6–1.4 wt.%) were prepared for further research.

This work succeeds the previous one on similar systems [24]. The correlation between the catalysts photoactivity, the energies of band gap and the energies of holes and electrons formation will be further discussed. In this case, the photocatalytic decomposition of ammonia was chosen as a model reaction. Ammonium hydroxide was chosen as the ammonia source.

2. Experimental

2.1. Preparation of cerium doped TiO₂ photocatalysts

The parent TiO₂ and a set of cerium doped TiO₂ photocatalysts with 0.6–1.4 wt.% of Ce were prepared via sol–gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane in combination with calcination [25,26]. Titanium(IV) isopropoxide (Ti(OCH(CH₃)₂)₄, purity >97%, Aldrich) and cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, Aldrich) were used as metal cations sources. For TiO₂ synthesis, the molar ratio of cyclohexane: Triton X-114:H₂O:Ti(OCH(CH₃)₂)₄ was kept 11:1:1:1 [25]. For the synthesis of Ce-doped TiO₂ (0.6, 1.2 and 1.4 wt.% of Ce), the molar ratio of cyclohexane: Triton X-114:H₂O:Ce(NO₃)₃·6H₂O+Ti(OCH(CH₃)₂)₄ was also 11:1:1:1, the appropriate amount of Ce(NO₃)₃·6H₂O was always dissolved using 3.5 ml of anhydrous ethanol [26]. The prepared homogeneous transparent sols were poured in a thin layer on Petri's dishes and left for 48 h on air at ambient temperature and pressure for gelation. The sols converted into rigid transparent yellow-colored gels. The titania and cerium doped titania gels were thermally treated at 350 °C for 4 h and then up to 500 °C for another 2 h with heating rate 3 °C/min in order to produce powder photocatalysts. All prepared solids were sieved to the particle size <0.160 mm.

2.2. Characterization of photocatalysts

Chemical analysis of powder catalysts was done on an ARL 9400 XP sequential WD–XRF spectrometer. All peak intensity data were

collected under vacuum conditions using the software WinXRF. The analyzed powders were pressed into pellets about 0.6 mm thick and the diameter of 25 mm without any binding agent and covered with 4 μm supporting polypropylene film.

Nitrogen physisorption was performed on the automated volumetric apparatus NOVA2000e (Quantachrome Instruments, USA) after sample degassing at 105 °C for 24 h under the vacuum less than 1 Torr. The adsorption–desorption isotherms of nitrogen were measured at –196 °C. The specific surface area, S_{BET}, was calculated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p_0 range = 0.05–0.30 [27,28].

XRD powder diffraction patterns were measured using PANalytical MPD diffractometer in the conventional Bragg–Brentano setup, using Ni-filtered CuKα radiation, variable divergence and antiscatter slits, 0.04 rad axial Soller slits and PIXcel detector. NIST LaB₆ standard reference material (660a) was used for the instrumental broadening calibration. XRD data analysis, focused on determination of lattice parameters/cell volume and crystallite size, was done using the Rietveld/WPPM [29] implemented in the software MSTRUCT [30,31]. Models described in [32] were used.

UV–vis diffuse reflectance spectra of hydrated and granulated (0.25–0.50 mm) catalysts were measured in quartz cuvettes (thickness 5 mm) by using a GBS CINTRA 303 spectrometer (GBC Scientific Equipment, Australia) equipped with an integrating sphere covered by BaSO₄ layer as a standard. The spectra were recorded in the range of the wavelengths 200–900 nm (lamps switched at 350 nm) and the scan rate was 100 nm/min. The scan step was 1 nm and the width of monochromator slit was 2 nm. The reflectances were recalculated to the absorption using the Kubelka–Munk equation:

$$F(R_{\infty}) = (1 - R_{\infty})^2 / 2 \cdot R_{\infty}, \quad (1)$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer.

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 ($\Phi_{ref} = 4.3$ eV) provided by the manufacturer. During the measurements, the gradient of the peak-to-peak versus backing potential was set to 0.2, whereas the vibration frequency and amplitude was set to 120 Hz and 40 a.u. The final V_{CPD} value was an average of 60 independent points using two backing potentials. The measurements were carried out under atmospheric pressure and ambient temperature. Before the measurements the samples were pressed into pellets of 10 mm diameter using the 8 MPa pressure. The work function values were obtained from a simple relation $V_{CPD} = \Phi_{ref} - \Phi_{sample}$.

2.3. Photocatalytic tests

The photocatalytic decomposition of ammonia was carried out in a stirred batch annular reactor with a suspended catalyst illuminated by UV 8 W Hg pen-ray lamp with a peak intensity at 254 nm (Ultra-Violet Products Inc., USA, 11SC-1) situated in the center of the quartz glass tube. The reactor shell was made from stainless steel (Fig. 1). Ammonium hydroxide was chosen as the source of ammonia. The concentration of ammonia was 0.883 g/l. To create an inert atmosphere in the reactor and to remove soluble oxygen and nitrogen, argon (purity 5.0) was bubbled through the suspension. Due to this purging the concentration of ammonia decreased to 0.8274 g/l. The gas samples were discontinuously taken and H₂ and CH₄ were immediately analyzed on a gas chromatograph equipped with a TCD and FID (YL 6000 Young-Lin, Labicom). The columns used for the separation were Pora-plot Q and MolSieve. Another gas chromatograph (Agilent 7890 equipped with MolSieve column) was used for analyzing nitrous oxide which might be a possible product.

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