Photocatalytic Decomposition of Nitrous Oxide using TiO_2 and Ag-TiO_2 Nanocomposite Thin Films

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Abstract

TiO_2 and Ag-TiO_2 (0.05, 0.25 and 1 wt% of Ag) thin films were prepared by the sol-gel method. The prepared films were characterized using SEM-EDAX, XRD, Raman spectroscopy, atomic force microscopy and UV-Vis spectrometry. Photocatalytic decomposition of N_2O was performed in an annular batch reactor illuminated with an 8 W Hg lamp (254 nm wavelength). The photoreactivity of Ag-TiO_2 increases with the Ag amount to 0.25 wt% Ag. Further increase of Ag loading to 1 wt% Ag did not change N_2O conversion. The Ag particles deposited on the TiO_2 surface can act as electron–hole separation centers. The presence of water vapor and oxygen in the reaction mixture slightly improved N_2O conversion.

Key words: N_2O, Photocatalytic decomposition, Ag, TiO_2, Thin film

1. Introduction

N_2O is the third most important of the long-lived greenhouse gases in terms of global warming, accounting for 6.2% of the total global radiative forcing. Although it only comprises 320 parts per billion of the earth's atmosphere, its contribution to global warming is important, as it has a GWP_{100} (global warming potential time horizon of 100 years) nearly 300 times greater than that of CO_2 [1].

The largest anthropogenic source of nitrous oxide (N_2O) is agriculture (use of synthetic nitrogen fertilizers) and cattle breeding. N_2O is also emitted from the industrial production of nitric acid and of adipic acid, fossil fuel combustion and biomass burning. An important message is that N_2O emission has been identified for aged three-way catalysts. N_2O is also formed in soils and oceans throughout the world by a natural biogeochemical nitrogen cycle: the microbial processes of nitrification of ammonium and denitrification of nitrate. As they are predominantly biogenic in origin, N_2O emissions are difficult to estimate, but the quantity of this gas has virtually doubled since the beginning of the industrial age. The concentration

of N_2O in the atmosphere continues to increase (0.2–0.3% yearly), and this increase appears to be caused mainly by anthropogenic activities [1]. Photocatalytic decomposition of N_2O under UV irradiation on semiconductor photocatalysts (Eq. 1) is one of the candidate methods for its removal.

$$N_2O \xrightarrow{hv,catalyst} N_2 + 1/2\ O_2 \qquad\qquad (1)$$

N_2O can be reduced by the electrons generated by UV irradiation on semiconductor photocatalysts. Since photocatalysts are suitable for treatment of low-concentration gases and are used at room temperature with light as the energy source, photocatalytic decomposition has many advantages: the concentration process is not necessary, the reaction conditions are mild, and furthermore, when sunlight would be utilized, it will lead to energy savings. While thermal catalytic decomposition of N_2O (without light) is suitable mainly for N_2O abatement from waste gases from industry and combustion, N_2O photocatalytic decomposition might help to reduce its concentration in the atmosphere caused by other sources. The first field experiment of decreasing the N_2O concentration in a pig house by coating the walls with TiO_2, carried out in 2008 [1], showed that this method is feasible in real conditions.

In comparison with thermal catalytic decomposition of N_2O, there are only a few papers dealing with this. These researchers focused on Cu and Ag ion-exchanged powder zeolite catalysts [2, 3], and Cu^I ion anchored on various oxides ($SiO_2.Al_2O_3$, Al_2O_3, SiO_2) [4-5].

Also, the most famous TiO_2 photocatalyst was tested for N_2O photocatalytic decomposition [6]. TiO_2 may be doped or combined by non-metallic ions, metallic ions, and other semiconductors. Improved photocatalytic activity was observed after the doping of TiO_2 by Pt [6] and Ag [7, 8]. Noble metals deposited on or doped into the TiO_2 lattice provide high Schottky barriers and act as electron traps which facilitate e^- - h^+ separation and promote interfacial electron transfer processes. These phenomena enhance the photocatalytic activity of TiO_2 through the decreasing of the carriers' recombination rate.

However, some noble metals such as Pt, Pd, Rh, and Au are too expensive to be used on an industrial scale. Since silver is not as expensive, research on Ag-doped TiO_2 has a significant practical value. Silver is suitable for industrial applications due to its low cost and easy preparation. Moreover, silver has been observed to play an important role in increasing the photocatalytic stability of TiO_2 as well [9].

In our recent work, Ag-enriched TiO_2 powders with various Ag loading (0.7–5.2 wt%) were prepared by a sol-gel process controlled in the reverse micellar environment, and successfully used for N_2O photocatalytic decomposition to oxygen and nitrogen [8]. The

highest N_2O conversion after 24 hours was reached in the presence of 3.4 wt% Ag-TiO$_2$ catalyst.

Recent investigations on TiO$_2$ photocatalysis are oriented towards the photocatalyst immobilization in the form of a thin film. The immobilization of the photocatalyst in the form of a thin film overcomes the drawbacks encountered with the powder form of catalyst: (1) the difficulty of separating inactive catalysts, (2) the difficulty of applying them to continuous flow systems, and (3) the intendancy of the particle catalysts to aggregate [10].

Ag is one of the most promising transition metals for the improvement of photocatalytic activity of TiO$_2$ thin film [11] and has been investigated extensively in the literature e.g. for the degradation of organic pollutants [11-15] or bacteria degradation [16]. However, any thin films have not yet been tested for N_2O photocatalytic decomposition. For that reason we decided to prepare TiO$_2$ and Ag-modified TiO$_2$ thin films and investigate them for this reaction. To simulate real conditions, the effect of oxygen and water vapor on the N_2O conversion was also tested as it has been studied only rarely.

2. Experimental

2.1. TiO$_2$ and Ag-TiO$_2$ thin film preparation

Films i) TiO$_2$ and ii) Ag-TiO$_2$ were prepared. The synthesis of the TiO$_2$ film was performed according to the procedure described by Zita et al. [17]. In this procedure, two independent solutions A and B are prepared. Solution A consists of 36 ml titanium tetraisopropoxide (TTIP, Sigma Aldrich) and 50 ml of anhydrous ethylalcohol (EtOH, Lachema), and solution B consists of 50 ml EtOH, 10 ml ethyl acetoacetate (EA, Merck) and 8.5 ml of concentrated HCl (Lachema). Solution A was dropwise added into the stirred solution B.

The sol for preparation of Ag-TiO$_2$ film was prepared using a previously slightly modified procedure based on the addition of the appropriate amount of the AgNO$_3$ (to give 0.05, 0.25 and 1 wt.% of Ag in final sol) into solution A under stirring. Both sols for preparation of TiO$_2$ as well as Ag-TiO$_2$ films were stirred for 24 hours using an electromagnetic stirrer. The prepared sol was dip-coated using COATER5 (idLAB) on the microscopy slide glass tubes (lengh of 10 cm, i.d. of 4 cm, Marienfield). The coating parameters were: dipping speed 20 cm/min, a delay of 3 s, and withdrawing speed 6 cm/min. The samples were calcined at 500°C for 1 h. A coated surface of 124.5 cm^2 is expected for each glass tube.

2.2. Characterization of TiO₂ and Ag-TiO₂ thin films

Various techniques were used to characterize the prepared layers. The scanning electron microscope (SEM) Philips XL30 with energy dispersive X-ray microanalysis (EDAX) was utilized for determination of the Ag content in prepared films.

Transmission spectra of the thin films deposited on the microscope slides were recorded using fiber optic spectrometer USB4000 (OceanOptics), and a deuterium tungsten halogen source DT-MINI-2GS (OceanOptics) was used as a light source. The pure microscope slide calcined for 1 h at 500°C was used for setting the background.

Raman spectra of all samples were obtained using a Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France). Raman spectra were acquired with a 532 nm excitation laser source, 100x objective and grating with 600 gr./mm. Achieved Raman spectra were processed by LabSpec software.

The atomic force microscope (AFM) SOLVER NEXT (NT-MDT) operating in the semicontact mode and PPP-NCHR probes (Nanosensors) were utilized for observation of the topography of the as prepared and calcined thin films. The data were evaluated using software Gwyddion ver. 2.26.

2.3. Photocatalytic reactivity experiments

Photocatalytic N₂O decomposition was carried out in a homemade apparatus at an ambient temperature. The glass tube with a catalyst thin film was inserted in the batch annular reactor (volume of 450 ml). The reactor was filled with 0.1 molar% N₂O/He mixture and illuminated by an 8 W Hg lamp with a peak light intensity at 254 nm. Water vapor (0.8 molar %) and oxygen (6.5 molar %) were added to the reaction mixture in some experimental runs. During the reaction, pressure and temperature inside the reactor were monitored. Gas chromatograph with thermal conductivity detector (GC/TCD) equipped with the Molsieve and HP Poraplot Q columns was used for the analysis of N₂O and O₂/N₂ molar ratio. The N₂O concentration level was measured before switching on a UV lamp, and during the irradiation. The reproducibility of photocatalytic experiments was verified by repeated tests.

The N₂O conversion was determined according to Eq. 2 provided that the total pressure in the reactor could be considered as constant due to low N₂O concentration.

$$X_{N_2O} = \frac{x^o_{N_2O} - x_{N_2O}}{x^o_{N_2O}}$$

$$(2)$$

Where $x^o_{N_2O}$, x_{N_2O} is the N_2O concentration at the beginning of reaction (t = 0) and at different times during the photocatalytic reaction, respectively.

3. Results and discussion

3.1. Characterization of TiO_2 and Ag-TiO_2 thin films

Chemical analysis of Ag-TiO_2 films using EDAX analysis confirmed the Ag content to be 0.05, 0.25 and 1 wt.%, respectively. SEM images (Fig. 1) show all the samples of the anatase film on the glass microscope slides to have amorphous character with crystalic salts based on various chlorides on the surface of the film. The chlorides come from the synthesis of the film.

Fig. 2 shows the dependency of transmittance of prepared films on wavelength of irradiation. The run of the registered transmittance spectra is typical for thin layers consisting of the TiO_2. It is evident that the transmittance of the TiO_2 layers doped with silver reaches slightly higher values in comparison to pure TiO_2 layer and TiO_2 layer with the lowest content of Ag. The strong decrease in transmittance of optical spectra for all samples was evident in the the UV region proving the semiconducting properties of the TiO_2 and Ag-TiO_2 films due to the existence of the band gap. The strong absorption of irradiation starts to occur below the wavelength 350 nm (~3.5 eV) for sample 0.05%Ag-TiO_2, below 360 nm (~3.4 eV) for sample TiO_2 and below 370 nm (~3.4 eV) for samples 0.25%Ag-TiO_2 and 1%Ag-TiO_2. The estimated band gap energies are slightly higher in comparison with the energy of pure TiO_2 in anatase form ~ 3.2 eV. The higher band gaps observed at our samples could be associated with the nano-crystalline nature of the prepared films.

Fig. 3 shows the Raman spectra in the range of 100–700 cm^{-1} of Ag-TiO_2 films annealed at 500°C. An intensive band at 137 cm^{-1} and low intensity bands around 190, 390, 540, and 635 cm^{-1} verify the TiO_2 presence in the anatase form [18]. Compared to the literature, the most intense peak of the anatase single crystal at 144 cm^{-1} [19] was in the Raman spectra of the calcined films shifted towards a lower frequency. This shift may be attributed to the higher roughness of the Ag-TiO_2 thin film in comparison with anatase single crystal as was also observed by Medina-Valtierra et al. [20]. No bands belonging to the rutile form were observed. The main difference evident from the Raman spectra is in the width of the most intense band at 137 cm^{-1}. Full width half-maximum (FWHW) determined for this band was the highest for the pure TiO_2 sample (45.8 cm^{-1}) while the Ag-modified samples

have much lower values of FWHW (down to 22.8 cm^{-1}). This tendency may show the Ag-modified samples to have less amorphous character compared to the pure TiO_2 sample.

The surface topography of the original and calcined thin films reveals the 3D images obtained using semi-contact AFM. Surface topography of the thin film assigned as 0.05% Ag-TiO_2 in non-calcined state and after its 1 hour calcinations at 500°C is shown in Fig. 4 a, b, respectively. Surface topography of the thin films assigned as 0.25% Ag-TiO_2 and 1% Ag-TiO_2 in non-calcined state and after its 1 hour long calcinations at 500°C are shown in Figs. 4 c, d and e, f. The determined values of the root mean square height of the surface (Sq) of the prepared thin films are summarized in Table 1.

The effect of the silver on the properties of the TiO_2 films is evident from the AFM images. All of the non-calcined films show porous structure, when regularly distributed holes appeared mainly in the case of the films containing silver, also apparent porosity is higher in the case of the silver doped films. After the calcination at 500°C, the surface characteristic of all of the films changed. The surface roughness of the pure TiO_2 thin film increases after the calcination, whereas the surface roughness of the thin film with Ag decreases after the calcination. It is also evident, that the higher the content of the silver, the lower the value of the root mean square height (Sq) of the surface (see Table. 1). It can be considered that the presence of the silver has an inhibitory effect on the TiO_2 grains growth.

3.2. The photocatalytic decomposition of N_2O

The effect of irradiation time on the photocatalytic decomposition of N_2O was studied for TiO_2 and Ag-TiO_2 thin films during 0–24 h (Fig. 5). The gradual increase of N_2O conversion with increasing Ag content was observed; the highest N_2O conversions of 45% over samples containing 0.25% and 1% Ag in reaction time of 24 hours were reached. N_2/O_2 molar ratio close to the expected value of 2 confirmed that N_2O decomposes only to nitrogen and oxygen. An integral form of material balance of batch reactor with ideal mixing working in isothermal and isobaric regime and 1st order kinetic equation $r = k\, c_{N_2O}$ were used for data processing:

$$\ln \frac{1}{1-X} = k\ \frac{S_{cat}}{V} t$$

(1)

Where c_{N_2O} is a concentration of N_2O (mol cm^{-3}), k is kinetic constant (cm^3 h^{-1} cm$_{cat}^{-2}$), r is reaction rate (mol cm$_{cat}^{-2}$h^{-1}), t is reaction time (h), V is volume of reactor (cm^3), S_{cat} surface of catalyst film (cm$_{cat}^2$) and X is N_2O conversion (-). Evaluation of the kinetic

confirmed that the reaction kinetics was well described by 1st rate order which is in agreement with plausible reaction mechanisms published recently on Ag-TiO$_2$ photocatalyst powders [8]. The effect of silver doping on the kinetic constants k of N$_2$O photocatalytic decomposition is shown in Table 1. The photoreactivity of Ag-TiO$_2$ increases with Ag amount to 0.25% Ag. Nevertheless, further increase of Ag loading (1%) enhances the kinetic constant only slightly in accordance with measured N$_2$O conversions. Thus, the range 0.25% - 1% Ag loading seems to be the optimal amount with respect to a catalyst's activity (the highest kinetic constant).

The Ag loading content has an important effect on the photocatalytic activity. Too much Ag loading content may result in a photohole trapping effect. Due to the fact that the Ag particles and clusters on the TiO$_2$ nanoparticles are relatively negative charged due to the formation of the Schottky barriers, the photoholes in the interfacial region of the TiO$_2$film may be trapped by the negatively charged Ag particles and clusters before they react with N$_2$O. This trapping effect was neglectable when the Ag concentration is below 1wt.%, and the Schottky barrier predominantly promoted the TiO$_2$ charge separation efficiency. The TiO$_2$ photocatalytic activities, therefore, increased with the increasing Ag concentration. With the Ag concentration increasing beyond this treshold, however, the trapping effect became prevailing and the decrease of photocatalytic activity is expected. The decline in the photocatalytic activity can also be associated with the change of the reaction site density. As the Ag$^+$ concentration increased beyond treshold value, the coverage of Ag on TiO$_2$ surface will increase. In other words, the density of reaction sites (for adsorption of UV light, to produce photohole and photoelectrons) at the surface of the resulting film would decrease. Consequently, the TiO$_2$ photocatalysis is depressed [21].

The effect of oxygen and water vapour presence on N$_2$O photocatalytic decomposition was tested over the most active 1%Ag-TiO$_2$ photocatalyst. Oxygen and water vapour are always present in atmosphere together with N$_2$O and it is known that they often inhibit the rate of N$_2$O thermal decomposition, mainly due to the competitive adsorption on active sites [22]. In N$_2$O photocatalytic decomposition, a completely opposite effect was observed (Fig. 6): higher N$_2$O conversion corresponding to the higher 1st order rate constant was obtained in the presence of O$_2$ and H$_2$O in comparison with N$_2$O photocatalytic decomposition in inert gas (Table 1). It could be caused by reduction of N$_2$O by atomic hydrogen formed by the photoreduction of water on an Ag-TiO$_2$ photocatalyst [7].

Increase of N$_2$O conversion in the presence of water vapour e.g. over TiO$_2$ modified by Ag, Cu, Ru and Pt [6], as well as a decrease of N$_2$O conversion e.g. over Ag-TiO$_2$ [7] was published for N$_2$O photocatalytic decomposition. It depends on the photocatalyst type and on

its properties. If the splitting of water proceeds simultaneously with N_2O photocatalytic decomposition, an increase of N_2O conversion can be expected.

Reducing agents such as CO, NH_3 or methanol have been described for N_2O photocatalytic reduction in literature [6, 7, 23]. The necessity of reductant storage, dosing and undesirable products of its oxidation are among the main disadvantages. From this point of view, water as a reductant seems to be favorable. However, further research needs to be performed for broadening the light spectrum range allowing the adsorption of the solar energy.

4. Conclusions

TiO_2 and Ag-TiO_2 thin films were successfully prepared by dip-coating on glass tubes and showed promising photocatalytic activity for N_2O decomposition. The gradual increase of N_2O conversion with increasing Ag content was observed, and samples containing 0.25 wt% and 1 wt% Ag were the most active. Moreover, a slight increase in N_2O conversion in the presence of water vapor and oxygen was observed. Atomic hydrogen formed by the photoreduction of water on an Ag-TiO_2 photocatalyst acts as a reducing agent. Reaction kinetics was well described by 1st rate. The Ag particles deposited on the TiO_2 surface can act as electron–hole separation centers, retarded their recombination and increased N_2O conversion.

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