Selective photocatalytic degradation of azodyes in NiO/Ag₃VO₄ suspension

Xuexiang Hu and Chun Hu*

Abstract

BACKGROUND: This work deals with the development of an active heterogeneous catalyst for selective organic synthesis under both visible light and UV irradiation to utilize efficiently solar light. Very few studies have been reported on the selective photooxidation performance of multimetal oxide materials under visible light irradiation. The photocatalytic degradation of azodyes was investigated systematically in aqueous NiO/Ag₃VO₄ dispersion under visible light irradiation.

RESULTS: The catalyst NiO/Ag₃VO₄ showed high activity and selectivity for the photodegradation of the nonbiodegradable azodyes acid red B, reactive brilliant red X-3B, and acid orange 7. From total organic carbon (TOC), Fourier transform infrared spectroscopy (FTIR), and gas chromatography/mass spectroscopy analyses, the tested azodyes were selectively oxidized into aromatic and aliphatic acids without any decrease of TOC. The high photooxidation selectivity also applied to UV light irradiation. Electron spin resonance and radical scavenger studies suggest that the anionic superoxide radical O₂^{•-} was the predominant active species in the photocatalytic reaction.

CONCLUSION: The selectivity of NiO/Ag₃VO₄ for the oxidation of azodyes was not affected by the energy of light (UV and visible light). This approach allows effective controlled oxidation but avoids undesirable mineralization into CO₂ and H₂O.

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Keywords: Photocatalyst; Selective degradation; Azodyes; Visible light

INTRODUCTION

Photocatalysis has received enormous attention in recent years because of its application in organic synthesis,^{1,2} and in the abatement of pollutants in water or in air,^{3,4} since the reaction can be driven by sunlight at near ambient temperatures and pressure using molecular oxygen as an oxidant.^{5,6} TiO₂ has been extensively investigated for its application in several fields and in particular for its activity in the oxidative photodegradation of a range of organic substrates.^{7,8} However, TiO₂ can only exhibit photocatalytic activity under UV irradiation. UV light accounts for only ca 4% of the total solar energy whereas visible light accounts for 43% and is the principal component of indoor artificial illumination. Therefore, the development of an active heterogeneous catalyst under both visible light and UV irradiation to utilize efficiently solar light is critical. Multimetal oxide materials as a series of novel photocatalysts have been intensively studied since Zou *et al.*⁹ recorded water splitting to H₂ and O₂ in stoichiometric amounts over NiO_x/In_{0.9}Ni_{0.1}TaO₄ under visible light irradiation.^{10–13} Many investigators have reported that organic pollutants can be mineralized by heterogeneous photocatalytic oxidation using TiO₂^{14,15} or multimetal oxide materials such as Bi₂WO₆.¹⁰ However, complete mineralization needs prolonged irradiation, which impedes the practical application of photocatalytic degradation in water treatment. It should be noted that a high degree of mineralization is not necessarily desirable in a photochemical reaction. In a photocatalytic process as pre-treatment for activated sludge treatment, for example, it is much more important to selectively oxidize the reactants than to convert them to CO₂ and H₂O.¹⁶ In addition, selective oxidation of compounds without

mineralization is very attractive in organic synthesis for other substrates.¹⁷ Recently, we have synthesized Ag₃VO₄ powders by a hydrothermal method with NiO introduction by impregnation.¹⁸ In the present study, the photocatalytic degradation of azodyes was investigated systematically in an aqueous NiO/Ag₃VO₄ dispersion under visible light irradiation. NiO/Ag₃VO₄ was found to exhibit high selectivity for azodyes photooxidation under visible light and UV irradiation. Azodyes could be readily bleached in a short time but mineralization did not occur as indicated by the near 0% TOC removal. Anionic superoxide O₂^{•-} radicals, detected by electron spin resonance (ESR) analysis, are responsible for the selective photooxidation of azodyes.

EXPERIMENTAL

Materials and reagents

Spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma Chemical Co. and stored at –20 °C. Azodyes acid red B (ARB), acid orange 7 (AO7) and reactive brilliant red X-3B (X-3B) were supplied by the Shanghai Chemical Co. Hexamethyldisilazane and chlorotrimethylsilane were purchased

* Correspondence to: Chun Hu, State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China. E-mail: huchun@rcees.ac.cn

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

from Aldrich and used as received. All other chemicals were analytical grade and used without further purification. Deionized and doubly distilled water was used throughout this study.

Catalyst preparation

Based on a previous report,¹⁸ Ag_3VO_4 was prepared by a hydrothermal process at 160°C for 48 h. Subsequently, NiO was loaded by impregnation where 0.5 g Ag_3VO_4 was placed in 0.1 mol L^{-1} $\text{Ni}(\text{NO}_3)_2$ aqueous solution and evaporated at 70°C . Then the dried powder was calcined at 300°C for 1 h to obtained $\text{NiO}(2\%(\text{w/w}))/\text{Ag}_3\text{VO}_4$.

Catalyst characterization

Elemental composition and content in $\text{NiO}/\text{Ag}_3\text{VO}_4$ was measured using a scanning electron microscope (S-3000N, Hitachi, Japan) equipped with energy dispersive X-ray spectroscopy (EDX). UV–visible diffuse reflectance spectra of the samples were recorded on a UV–vis spectrophotometer (Hitachi UV-3010) with an integrating sphere attachment. The range analyzed was 250–800 nm, and BaSO_4 was the reflectance standard. XPS data were taken on an AXIS–Ultra instrument (Kratos, England) using monochromatic Al $K\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV. Ion chromatography (IC) (LC20 ion chromatograph, Dionex, USA) was used to assay the quantity of SO_4^{2-} formed in the photodegradation of the ARB. ESR spectra were obtained using a ESP 300E (Bruker, Germany) electron paramagnetic resonance spectrometer equipped with a quanta-Ray Nd: YAG laser system as the irradiation light source ($\lambda = 532 \text{ nm}$). The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW.

Procedure and analyses

The light source for photocatalysis was a 350-W Xe arc lamp (Shanghai Photoelectron Device Ltd). Light passed through a water filter and a UV cutoff filter ($\lambda > 420 \text{ nm}$, Shanghai Seagull Coloured Optical Glass Co., Ltd) and then was focused onto a 100-mL beaker. The reaction temperature was maintained at 25°C . The average light intensity was 2.5 mW cm^{-2} . In the UV irradiation experiment, UV source was a 375 W Hg lamp with a maximum emission at 365 nm. The average UV output intensity was 7.8 mW cm^{-2} at 365 nm as determined at the center of the photoreactor. Three non-biodegradable azodyes (ARB, AO7, X-3B) were selected as model chemicals to evaluate the activity and properties of the catalyst. The structure of selected azodyes are shown in Scheme 1. In a typical experiment, aqueous suspensions of azodyes (60 mL , 50 mg L^{-1}) and 0.1 g of catalyst powders were placed in the beaker. Prior to irradiation, the suspensions were magnetically stirred in dark for ca. 30 min to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under room air equilibrated conditions. At given irradiation time intervals, 3 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size $0.22 \mu\text{m}$) to remove the catalyst particulates for analysis. The filtrates were analyzed by recording variations at the wavelength of maximum absorption in the UV–vis spectra of dyes using model 752N spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., China). Total organic carbon (TOC) of the solution was analyzed with a 8000 TOC analyzer (Phoenix, USA). The SO_4^{2-} ions were determined by ionic chromatography (Dionex Series 4500!).

Figure 1. Temporal course of the photodegradation of ARB (50 mg L^{-1} , 60 mL) in aqueous dispersions containing 1.67 g L^{-1} of catalysts: (a) $\text{NiO}/\text{Ag}_3\text{VO}_4$ in the dark; (b) no catalyst, (c) $\text{NiO}/\text{Ag}_3\text{VO}_4$ under visible light irradiation.

Samples for gas chromatography/mass spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FT-IR) analysis were prepared by the following procedures. The suspensions at different irradiation times were filtered to remove catalyst particles. The solutions were evaporated using a freeze-dried method. For FT-IR measurement, the dry residue was supported on KBr pellets. The infrared spectrum was recorded on a FT-IR spectrophotometer (Nicolet 5700, USA). For GC-MS analysis, the residue was trimethylsilylated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane.¹⁹ The reaction was carried out in a 1.5 mL plastic vial. The mixture was shaken vigorously for ca 1 min and was then allowed to stand for 5 min at room temperature. Precipitate was separated by centrifugation prior to chromatographic analysis. GC-MS analysis was carried out on an 6890GC/5973MSD (Agilent, USA) with a DB-5 MS capillary column. The temperature program of the column was as follows: at 50°C , hold time = 20 min; ramp from 50 to 280°C at 8°C min^{-1} .

RESULTS AND DISCUSSION

Characterization of $\text{NiO}/\text{Ag}_3\text{VO}_4$

The composition of the $\text{NiO}/\text{Ag}_3\text{VO}_4$ was analyzed using EDX. The concentration of Ni was 6.6% (w/w) according to the EDX data, while based on the dosages of $\text{Ni}(\text{NO}_3)_2$ and Ag_3VO_4 , the concentration of Ni in Ag_3VO_4 was ca 2% (w/w), lower than the experimental value. This indicates that most NiO was supported on the surface of Ag_3VO_4 . Determination of the oxidation state of the doped nickel was carried out by measuring the Ni 2p_{3/2} binding energy (BE) with XPS. The BE at 854.2 eV was assigned to NiO. The optical absorption spectra of Ag_3VO_4 showed a visible-light absorption band at 400–580 nm. $\text{NiO}/\text{Ag}_3\text{VO}_4$ exhibited the same absorption edge as Ag_3VO_4 . However, the $\text{NiO}/\text{Ag}_3\text{VO}_4$ specimen showed greater light attenuation throughout the visible wavelengths consistent with the gray color of the catalyst.

Selective photooxidation of azodyes in $\text{NiO}/\text{Ag}_3\text{VO}_4$ system

Figure 1 shows the variations in the concentration of ARB under different visible light illuminated catalysts. As a reference, ARB photolysis was also performed under the same conditions. Neither visible light nor $\text{NiO}/\text{Ag}_3\text{VO}_4$ in the dark showed any activity for ARB degradation (curves a and b). In contrast, ARB was decolorized by 80% in $\text{NiO}/\text{Ag}_3\text{VO}_4$ suspension after 20 min of irradiation (curve c). These results indicated that the dye self-photosensitization

Scheme 1. Structures of ARB, X-3B, and AO7.

Figure 2. Cycling runs in the photocatalytic degradation of ARB in the presence of $\text{NiO}/\text{Ag}_3\text{VO}_4$ under visible-light irradiation, $\text{NiO}/\text{Ag}_3\text{VO}_4$ (1.67 g L^{-1}); addition of ARB (50 mg L^{-1} , 100 mL per run).

Figure 4. Decolorization and TOC removal of azo-dye solution in $\text{NiO}/\text{Ag}_3\text{VO}_4$ suspension under UV light irradiation. (a) (d) ARB, (b) (e) AO7, (c) (f) X-3B.

Figure 3. Decolorization and TOC removal of the solution, SO_4^{2-} ions formation during the degradation process of ARB in $\text{NiO}/\text{Ag}_3\text{VO}_4$ suspension under visible light irradiation ($\lambda > 420 \text{ nm}$).

process and absorption process could be ignored, and the photocatalytic step was the predominant process in the system of $\text{NiO}/\text{Ag}_3\text{VO}_4$ /visible light. Consecutive oxidations of ARB (5 cycles) in the same solution showed that the catalyst had good stability, as shown in Fig. 2.

Figure 3 shows TOC removal of the solution and the formation of inorganic ions with exposure time during the photodegradation of ARB under visible light irradiation. Obviously, the formation of SO_4^{2-} increased after the ARB was completely decolorized, and ca 90% of the total sulfur content was converted into SO_4^{2-} ions after 12 h irradiation. The formation of SO_4^{2-} also verified that the photocatalytic process occurred in the visible light illuminated $\text{NiO}/\text{Ag}_3\text{VO}_4$ suspension system. However, the TOC showed little change over 30 h of irradiation, i.e. no significant change in the total organic content before and after photo-decolorization of ARB. This suggests that the process was a selective oxidation rather than a mineralization.

In order to understand the selectivity of $\text{NiO}/\text{Ag}_3\text{VO}_4$ for the oxidation of ARB, the photooxidation of ARB was carried out in $\text{NiO}/\text{Ag}_3\text{VO}_4$ under different irradiation light sources. After 30 h of visible irradiation, the reaction system was subsequently irradiated by UV light (375 W Hg lamp) but neither further oxidation nor mineralization was observed. The same reaction was carried out under UV irradiation where TOC was largely unaltered after 6 h of irradiation, as shown in Fig. 4. These observations illustrate that the photocatalytic selectivity of $\text{NiO}/\text{Ag}_3\text{VO}_4$ did not depend on the excitation wavelength. The processes of photooxidation of other azodyes X-3B and AO7 were also performed in $\text{NiO}/\text{Ag}_3\text{VO}_4$

Figure 5. Photodegradation of different azodyes (50 mg L⁻¹, 60 mL) in aqueous dispersions containing 0.1 g NiO/Ag₃VO₄ under visible light irradiation ($\lambda > 420$ nm).

Figure 6. Changes of FT-IR spectra during the photodegradation of ARB with NiO/Ag₃VO₄ under visible light irradiation ($\lambda > 420$ nm).

Figure 7. DMPO spin-trapping ESR spectra recorded at ambient temperature in methanol dispersion. (a) NiO/Ag₃VO₄; (b) NiO/Ag₃VO₄ with SOD under irradiation of 532 nm; (c) NiO/Ag₃VO₄ in dark.

suspension under otherwise identical conditions. The two azodyes were also degraded efficiently without any decrease of TOC under UV irradiation (Fig. 4) or visible light (Fig. 5). This provides sufficient evidence that the NiO/Ag₃VO₄ photocatalytic system possessed high selectivity for the photooxidation of azodyes, under visible light or UV light irradiation.

FT-IR and GC-MS were used to monitor the generation of reaction intermediates during the photodegradation of ARB under

Table 1. Molecular structures of products formed in the photooxidation of ARB

Retention time/min	Identified intermediates	Molecular structure	<i>m/z</i> (relative abundance %)
40.55	acetic acid		75(100), 73(14), 76(7), 117(6)
44.95	phthalic acid		147(100), 75(45), 73(39), 295(20), 148(16), 149(11), 76(9), 221(7), 140(6)

visible light irradiation. It is important to characterize these by-products to confirm the selectivity of photooxidation. FT-IR spectra of the degraded solutions of ARB, after irradiation at various time intervals are shown in Fig. 6. The characteristic peaks of the azo bond ($-N=N-$, at 1504 cm⁻¹) and the benzene ring (at 1400–1600 cm⁻¹) of ARB disappeared, and the characteristic peaks at 1190 and 1279 cm⁻¹ due to the asymmetric stretching vibration of the $-SO_3Na$ group²⁰ also disappeared after 2 h of irradiation. The results indicate that the azo bond and the benzene ring were attacked and desulfuration occurred with decolorization of ARB. Meanwhile, several new peaks at 1760 and 1790 cm⁻¹, attributed to the stretching vibration of C=O groups of carboxylic acids, and at 924 and 836 cm⁻¹, assigned to the substituted benzene were generated, at 1132 cm⁻¹, assigned to the characteristic absorption of SO_4^{2-} , were generated after 2 h of irradiation. Moreover, their intensity increased with increasing irradiation time. The results of GC-MS further confirmed these results (Table 1). For the photodegradation of ARB, samples treated for 8 h and 30 h of irradiation were analyzed. All the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%. The main products included phthalic acid and acetic acid at 8 h of irradiation. After a further 30 h of irradiation, these products were still present, and no other product was formed. The same byproducts were also identified under UV light irradiation. For the degradation of X-3B and AO7, the main intermediates included both aromatic and aliphatic acids such as benzoic acid, phthalic acid and hexanoic acid (Table 2). These products did not undergo further oxidation when the reaction system was irradiated by UV light. These results indicate that the azodyes were highly selectively oxidized into aromatic and aliphatic acids such as phthalic acid, acetic acid, and hexanoic acid in visible light or UV illuminated NiO/Ag₃VO₄ system, and these intermediates could not be further oxidized. The high selectivity of NiO/Ag₃VO₄ in the oxidation of azodyes was not affected by the energy of light, perhaps related to the active species in the photocatalytic reaction.

Mechanism of selective photooxidation

In general, it is known that the photocatalytic reactions proceed mainly by the contributions of active oxygen species (ROS), such as $\cdot OH$, $O_2^{\cdot -}$ and H_2O_2 . ROS are essential for the degradation of pollutants in the process of photocatalysis. The ESR spin-trap technique (with DMPO) was used to detect the nature of the reactive oxygen species generated on the surface of catalysts under visible irradiation (Fig. 7). Upon visible light irradiation (532 nm),

Table 2. Molecular structures of products formed in the photooxidation of X-3B and AO7

Retention time/min	Identified intermediates	Molecular structure	m/z (relative abundance%)
8.76	hexanoic acid		75(100), 73(80), 173(27), 117(18)
24.66	benzoic acid		105(100), 77(90), 179(74), 135(44), 51(25), 75(14), 73(13), 180(10)
45.32	phthalic acid		147(100), 73(84), 148(16), 76(14), 295(10), 74(10), 149(8)

Figure 8. Photocatalytic degradation of ARB over NiO/Ag₃VO₄ particles (1.67 g L⁻¹) in N₂-saturated, O₂-saturated, or air-equilibrated solutions ($\lambda > 420$ nm).

six characteristic peaks of the DMPO-O₂^{-•} adducts were observed in suspensions of NiO/Ag₃VO₄ under visible light irradiation (curve a). No such signals were detected under dark conditions (curve c). This means that irradiation is essential for the generation of O₂^{-•} on the surface of the catalyst. In another control experiment, SOD was added into NiO/Ag₃VO₄ methanol suspensions under otherwise identical conditions. The signal of DMPO-O₂^{-•} adducts was not observed under visible irradiation since SOD scavenged O₂^{-•} (curve b). The results further confirmed that O₂^{-•} radicals were generated from NiO/Ag₃VO₄ systems. Furthermore, no DMPO-[•]OH signals were detected in NiO/Ag₃VO₄ dispersion under visible light irradiation. Additional examinations of the role of the O₂^{-•} radicals in the degradation of ARB were performed. The photocatalytic reactions were carried out under deoxygenated conditions (purging N₂), in the presence of air and 100% oxygen. As shown in Fig. 8, the degradation of ARB was drastically suppressed in the absence of oxygen. Apparently, oxygen plays an important role in trapping photogenerated e⁻, leading to the generation of O₂^{-•}. Moreover, a relatively small difference was observed between the air-equilibrated solution and continued O₂-purged conditions for the degradation of ARB. This implies that there was enough oxygen for the photodegradation of ARB under air-equilibrated conditions. As shown in Fig. 9, the addition of

Figure 9. Plotted degradation kinetics of ARB in the NiO/Ag₃VO₄ suspension (1.67 g L⁻¹) under visible irradiation on addition of (a) no scavenger added, (b) benzoquinone, (c) isopropanol, (d) methanol, (e) acetone. Scavenger concentration: 1 mmol L⁻¹.

benzoquinone (0.1 mol L⁻¹), which has been reported to be a very efficient trap for O₂^{-•},²¹ led to marked suppression in the photodegradation rate of ARB (curve b). When [•]OH scavengers,²² isopropanol, methanol and acetone, were introduced into the degradation systems, the degradation of ARB was not inhibited significantly (curves c–e). These experimental data suggested that the O₂^{-•} radical was the main active oxygen species in NiO/Ag₃VO₄ photocatalytic process with visible light irradiation. Therefore, the O₂^{-•} radical should be responsible for the selective oxidation of azodyes. Based on the complete decolorization and desulfuration of ARB, and the results of GC-MS analysis, it was found that the O₂^{-•} radical predominantly selectively attacked these substituent positions of naphthalene ring, leading to the scission of C–N and C–S bonds between the naphthalene ring and azo group, sulfonic group. Subsequently, the naphthalene ring was converted to phthalic acid, acetic acid. Similar phenomena were observed in the degradation of X-3B and AO7 where these substituent positions of benzene and naphthalene rings were highly selectively oxidized by the O₂^{-•} radical, resulting in the transformation of the benzene ring into hexanoic acid, and naphthyl rings into phthalic acid, benzoic acid. Furthermore, in visible light or UV illuminated NiO/Ag₃VO₄ system, these intermediates could not be further oxidized, indicating the high selectivity of the O₂^{-•} radical.

CONCLUSIONS

The NiO/Ag₃VO₄ photocatalytic system showed excellent reactivity and selectivity for the photooxidation of azodyes, under visible light or UV light irradiation. The energy of the light did not affect the selectivity of the NiO/Ag₃VO₄ photocatalytic system. The final products of the azodyes tested were simple organic acids. ESR and radical scavenger methodologies suggest that O₂^{-•} radicals are the main active oxygen species and are proposed to be responsible for the selective photooxidation of azodyes. NiO/Ag₃VO₄ is very promising for selective oxidation in organic synthesis or combined with biological treatment.

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