



Removal of nitrate and simultaneous hydrogen generation through photocatalytic reforming of glycerol over “in situ” prepared zero-valent nano copper/P25

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ABSTRACT

The photocatalytic reduction of nitrate to nitrogen and the simultaneous production of hydrogen was investigated over copper loaded titania (P25) nanoparticles using glycerol as sacrificial agent and UV-A/Vis radiation. The experiments demonstrated that total nitrogen (i.e., nitrate, nitrite, and ammonia) removal efficiencies over 93% were achieved for initial nitrate concentrations up to 150 mg/l. A parallel hydrogen production up to 14 μ M was recorded. Hydrogen generation was affected by nitrate reduction. The reaction rates were dependent on pH and both glycerol and nitrate starting concentrations in the mixture. However, a linear model can be used to describe the process for low concentration of nitrate and constant pH. The system showed a remarkable photoefficiency in decontamination of nitrate-containing solutions and concomitant hydrogen evolution. This study lays the foundation for the future development of numerical models able to predict the chemical behavior of simultaneous proton and nitrate reduction over solar photocatalytic reforming of organics.

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1. Introduction

Nitrate is one the most abundant ground and surface-water contaminants due to the massive use of fertilizers in agricultural activities, the disposal in the environment of large amounts of livestock manure, and the discharge of not efficiently treated wastewater [1]. Nitrate contamination is potentially hazardous to human health since it can cause methemoglobinemia (also known as “blue baby” syndrome), a highly fatal disease in babies under 6 months of age [2]. Nitrate ions are also considered endocrine disrupting chemicals with carcinogenic effects [3], leading to the production of nitrosamines in the human body [4]. For this reason, many Countries limited the nitrate content in drinking, ground, and surface water through specific regulations [5].

Conventional processes for the remediation of nitrate-contaminated ground waters such as biological processes, electro-kinetic denitrification, reverse osmosis, ion exchange and chemical reduction are often adopted or have been proposed in

the past, even if they show some drawbacks such as sludge production, relatively high operative costs and undesirable by-product formation [6].

Among all alternative technologies for nitrate removal in water, photocatalytic reduction processes are very promising for the possibility of exploiting solar energy to convert nitrate into non-toxic final by-products such as nitrogen gas instead of undesirable by-products (e.g., ammonia) that require additional treatments [49]. In particular, a large number of studies focused their attention on the photocatalytic activity of TiO₂ catalysts doped with metal ions conferring an increased nitrate removal efficiency with respect to bare TiO₂ (Table 1).

According to the literature, the presence of metal species in photocatalytic systems helps reduce the occurrence of photogenerated electrons/holes recombination and increase the charge-separation lifetime. Once transferred from the conduction band of TiO₂ to the metal, the photogenerated electrons are available for nitrate reduction.

Photocatalytic nitrate reduction is normally carried out under deaerated conditions and in presence of organic molecules acting as hole scavengers in order to increase the efficiency. As reported in Table 1, most of the papers found in the literature review were

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Table 1
Literature information on TiO₂-photocatalytic reduction of nitrate.

| Photocatalyst and preparation method | Hole scavenger | Photocatalyst concentration (g/l) | Photocatalyst activity ($\text{mmol}_{\text{NO}_3^-}/\text{min g}_{\text{photocatalyst}}$) | $\text{X}_{\text{NO}_3^-}$ and treatment time (% , h) | S_{N_2} (% , h) | Intermediates and final products (measured) | Ref |
|--|---|-----------------------------------|--|---|---------------------------------|--|------|
| TiO ₂ (P25, Hombikat UV100) (commercial) | Formic acid | 1 | – | 64–77 (n.r) | n.r. | NO ₂ [–] , NH ₃ | [7] |
| TiO ₂ (P25, Kronos-1002) (commercial) | Humic acids | 0.1 | – | 43 (66) | n.r. | n.r. | [8] |
| TiO ₂ (P25, Hombikat UV100) (commercial) | Formic acid | 0.4 | 1.6·10 ^{–1} | 100 (0.25) | 55–58 (0.25) | NO ₂ [–] , NH ₃ | [9] |
| TiO ₂ (Hombikat UV100) (commercial) | Formic acid | 1 | 9.20·10 ^{–4} | 87 (2) | 71 (2) | NO ₂ [–] , NH ₃ | [10] |
| TiO ₂ (P25) (commercial) | Oxalic acid | 2.5 | – | ≈ 3 (4) | n.r. | NO ₂ [–] , NH ₃ | [11] |
| TiO ₂ (P25) (commercial) | Formic acid | 1 | 8.80·10 ^{–4} | 27 (4) | 72 | NO ₂ [–] , NH ₃ | [12] |
| Cu-Pd/TiO ₂ (P25) (impregnation and calcination) | Formic acid | 15 | 2.2·10 ^{–3} | 100 (1) | n.r. | NO ₂ [–] , NH ₃ | [13] |
| Cu-Pd/TiO ₂ (P25) (impregnation and calcination) | Formic acid | 2 | 1.5·10 ^{–2} | 84 (4) | 83 (4) | NO ₂ [–] , NH ₃ | [14] |
| Pd/TiO ₂ (P25) (impregnation, reduction and calcination) | Formic acid | 0.6 | 5.0·10 ^{–2} | 70 (4) | 56 (0.33) | NO ₂ [–] , NH ₃ | [15] |
| Cu-Pd/TiO ₂ (impregnation, reduction and heating) | Formic, oxalic acids, methanol, ethanol | 0.5 | 5.4·10 ^{–2} | 18–98 (4) | 86–100 (1) | NO ₂ [–] , NH ₃ | [16] |
| Cu-Pd/TiO ₂ ; Cu-Pt/TiO ₂ ; Cu-Ni/TiO ₂ (P25) (co-impregnation/calcination) | Oxalic acid | 1 | 5.2·10 ^{–3} | 17 (2) | 19–100 (2) | NO ₂ [–] , NH ₃ | [17] |
| Ag/TiO ₂ (P25) (in situ or conventional photoreduction) | Formic acid | 1 | 2.2·10 ^{–1} | 72–98 (0.5) | 84–100 (0.5) | NO ₂ [–] , NH ₃ | [18] |
| Ag/TiO ₂ (P25) (in situ photoreduction) | Formic acid | 1 | – | 100 (n.r) | n.r. | NO ₂ [–] , NH ₃ | [19] |
| Ag/TiO ₂ (P25) (in situ photoreduction) | Formic acid | 1 | – | 100 (n.r) | n.r. | NO ₂ [–] , NH ₃ | [20] |
| Ag/TiO ₂ (P25) (photodeposition and calcination) | Formic acid | 0.1–1.2 | 7.4·10 ^{–3} | 65–90 (240) | n.r. | NO ₂ [–] , NH ₃ | [21] |
| Ag ₂ O/TiO ₂ ; Ag/TiO ₂ (P25) (chemical reduction) | Formic acid | 1 | 3.3·10 ^{–3} | 70–100 (4) | 37–85 (4) | NO ₂ [–] , NH ₃ | [12] |
| Cu/MgTiO ₃ -TiO ₂ (P25) (impregnation/calcination) | Sodium oxalate | 1 | 4.6·10 ^{–3} | 39 (2) | n.r. | NO ₂ [–] , NH ₃ | [22] |
| Cu/TiO ₂ ; Cr/TiO ₂ ; Zn/TiO ₂ (Hombikat UV100) (photodeposition) | Formic acid | 1 | 1.4·10 ^{–2} | 56–95 (2) | 50–95 (2) | NO ₂ [–] , NH ₃ | [10] |
| M/TiO ₂ (P25); M: Ag, Au, Co, Cu, Ni, Pd, Pd (impregnation, reduction and calcination) | Oxalic acid | 10 | – | 3–86 (3–6) | n.r. | NO ₂ [–] , NH ₃ | [23] |
| Cu-Pt/TiO ₂ (impregnation, reduction and calcination) | Benzene | 1 | 2.0·10 ^{–3} | 67 (4) | 20–80 (4) | NO ₂ [–] , NH ₃ | [24] |
| ZnO-TiO ₂ (Hombikat UV100) (photodeposition) | Formic acid | 1 | 1.42·10 ^{–2} | 92 (2) | 95 (2) | NO ₂ [–] , NH ₃ | [25] |
| M/TiO ₂ (P25, Hombikat UV100); M: Cu, Ag, Fe (impregnation or photodeposition) | Formic acid | 0.4 | 4.6·10 ^{–2} | 100 (0.25) | 11–96 (0.25) | NO ₂ [–] , NH ₃ | [9] |
| Bi/TiO ₂ (sol-gel, impregnation and calcinations) | Formic acid | 1 | 2.0·10 ^{–3} | 83 (3) | n.r. | NO ₂ [–] , NH ₃ | [26] |
| Au/TiO ₂ (P25, Hombikat UV100); (precipitation) | Oxalic acid | 0.2 | 2.5·10 ^{–2} | 52–60 (3) | n.r. | n.r. | [27] |

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