

Study on the Photocatalytic Reduction of Nitrate in Aqueous Solution by TiO₂-Based Photocatalysts

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ABSTRACT

The objectives of this work are to prepare TiO₂-based photocatalysts using the photodeposition method, and to evaluate the effectiveness of photoreduction of nitrate in water using modified photocatalysts. Ag and Cu were doped on and mounted on the substrate (Al₂O₃). The physical-chemical characteristics of the prepared photocatalysts were analyzed by ICP-AES, BET, SEM/EDX, and XRD. The experimental results showed that the specific surface area for the various photocatalysts is about 112~170 m²/g and the major crystalline type of TiO₂ is anatase. As for the photocatalytic reduction of nitrate, the Langmuir-Hinshelwood kinetic model can well describes the experimental results. The modified photocatalyst has a better effectiveness of photocatalytic reduction of nitrate, especially for the Cu-doped catalysts with a conversion of 99%. The optimum experimental condition are found to be pH 3, 0.1 g/L of photocatalyst loading, and using formic acid (HOOH) of the scavenger. Result also show that the nitrate convert to intermediates such as NO₂-; NH₃-N and urea, the production of NH₃-N and urea were affected by the formation rate of nitrite. This study confirmed that the energy-saving photocatalysts (BaF₂/TiO₂/Al₂O₃) can utilize the visible radiation and reduce nitrate, with the nitrate conversion of 10%.

Keywords : Photocatalytic Reduction ; Photocatalysts ; Al₂O₃ ; Nitrate ; Urea ; Kinetic model of reaction

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REFERENCES

1. 李彥志、徐寶崇、陳孝行，「奈米級含氮、鐵二氧化鈦之可見光光催化活性機制探討」，廢水處理技術研討會論文集，高雄大學，2007。林有銘，「奈米光觸媒」，科學發展，408期，2006。2. 林柏翔，「以改質光觸媒程序還原含六價鉻廢水之反應行為研究」，碩士論文，大葉大學環境工程學系，彰化，2007。3. 陳信宏，「改良型二氧化鈦光觸媒複合材料去除水溶液之染料之研究」，碩士論文，大葉大學環境工程學系，彰化，2007。4. 陳姿瑜，「金屬改質奈米二氧化鈦觸媒之研究與應用」，碩士論文，國立清華大學原子科學系，新竹，2006。5. 張雅婷，「輻射敏感型光觸媒複合材料的研製與性能探討」，碩士論文，國立清華大學原子科學系，新竹，2006。6. 張志玲，「原來光觸媒是這麼回事」，科學發展，373期，2004 7. 環保署環境檢驗所，「水中氨氮檢測方法 - 龔酚比色法」，網址 <http://www.niea.gov.tw>，2005年。8. 環保署環境檢驗所，「水中亞硝酸鹽氮檢測方法 - 分光光度計法」，網址 <http://www.niea.gov.tw>，2002。9. 環保署環境檢驗所，「水中硝酸鹽氮檢測方法 - 分光光度計法」，網址 <http://www.niea.gov.tw>，2006。10. 蘇俊鐘，NCHC奈米科學研究小組，網址 <http://nano.nchc.org.tw/dictionary/photocatalyst.html>，2003。11. Bems, B., Friederike, C.

and Robert, S., " Photoinduced decomposition of nitrate in drinking water in the presence of titania and humic acids ", Applied Catalysis B:Environmental, Vol.20, pp.155-163, 1999. 12. Douglas, L. A. and Bremner J. M., " Colorimetric determination of microgram quantities of urea ", Analyticalletter, Vol.3, pp.79-87, 1970. 13. Dey, G. R., Belapurkar, A. D. and Kishore K., " Photo-catalytic reduction of carbon dioxide to methane using TiO₂ as suspension in water ", Journal of Photochemistry and photobiology A: Chemistry, Vol.163, pp.503-508, 2004. 14. Guan, G., Kida, T. and Yoshida, A., " Reduction of carbon dioxide with water under concentrated sunlight using photocatalyst combined with Fe-based catalyst ", Applied Catalysis B: Environmental, Vol.41, pp. 387-396, 2003. 15. Guan, G., Kida, T., Harada, T., Isayama, M. and Yoshida, A., " Photoreduction of carbon dioxide with water over K₂Ti₆O₁₃ photocatalyst combined with Cu/ZnO catalyst under concentrated sunlight ", Applied Catalysis A: General, Vol.249, pp.11-18, 2003. 16. Gao, W., Jin, R., Chen, J., Guan, X., Zeng, H., Zhang, F. and Naijia Guan, " Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate ", Catalysis Today, Vol.90 , pp.331 – 336, 2004. 17. Hung, C. H. and Marinas, B. J., " Role of Water in the Photocatalytic Degradation of Trichloroethylene Vapor on TiO₂ Films ", Environmental Science and Technology, Vol.31, pp.1440-1445, 1997. 18. Hirose T., Maeno Y. and Himeda. Y., " Photocatalytic carbon dioxide photoreduction by Co(bpy)32+ sensitized by Ru(bpy)32+ fixed to cation exchange polymer ", Journal of Molecular Catalysis A: Chemical, V.193, pp.27-32, 2003. 19. Ferry, J. L. and Glaze, W. H., " Potocatalytic reduction of nitro organics over illuminated titanium dioxide:role of the TiO₂ surface ", Langmuir, Vol.14, pp.3551-3555, 1998. 20. Jin, R., Gao, W., Chen, J., Zeng, H., Zhang, F., Liu, Z. and Guan, N., " Photocatalytic reduction of nitrate ion in drinking water by using metal-loaded MgTiO₃-TiO₂ composite semiconductor catalyst ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.162, pp.585 – 590, 2004. 21. Jiang, F., Zheng Z., Xu Z., Zheng S., Guo Z. and Chen L., " Aqueous Cr(VI) photo-reduction catalyzed by TiO₂ and sulfated TiO₂ ", Journal of Hazardous Materials, Vol.134, pp.94-103, 2006. 22. Kishimoto, H., Takahama, K., Hashimoto, N., Aoi, Y. and Deki S., Journal of Materials Chemistr, Vol.8, pp.2019-2024, 1998. 23. Kuwabata, S., Yamauchi, H. and Yoneyama H., " Urea photosynthesis from inorganic carbon and nitrogen compounds using TiO₂ as photocatalyst ", Langmuir, Vol.14, pp.1899-1904, 1998. 24. Ku, Y., Lee, W. and Wang, W., " Potocatalytic reduction of carbonate in aqueous solution by UV / TiO₂ process ", Journal of Molecular Catalysis A: Chemical, Vol.212, pp.191 – 196, 2004. 25. Li, Y. and Wasgestian, F., " Photocatalytic reduction of nitrate ions on TiO₂ by oxalic acid ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.112, pp.255-259, 1998. 26. Mori, T., Suzuki, J., Fujimotoa, K., Watanabe, M. and Hasegawa, Y., " Reductive decomposition of nitrate ion to nitrogen in water on a unique hollandite photocatalyst ", Applied Catalysis B: Environmental, Vol.23, pp.283 – 289, 1999. 27. Mohapatra, P., Samantaray, S. K. and Parida, K., " Photocatalytic reduction of hexavalent chromium in aqueous ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.170, pp.189-194, 2005. 28. Mishra, T., Hait, J., Aman, N., Jana, R.K., Chakrav, S., " Effect of UV and visible light on photocatalytic reduction of lead andcadmium over titania based binary oxide materials ", Journal of Colloid and Interface Science, Vol.316, pp.80 – 84, 2007. 29. Nguyen, T., Wu, Jeffrey C.S., Chiou, C., " Photoreduction of CO₂ over Ruthenium dye-sensitized TiO₂-based catalyst sunder concentrated natural sunlight ", Catalysis Communications, Vol.9, pp.2073 – 2076, 2008. 30. Okamoto, K. I., Yamamoto, Y., Tanaka, H., Hanaka, M. and Itaya, A., Bulltein of the Chemistry Society Japan, Vol.58, pp.2015-2022, 1985. 31. Park, E. H., Jung, J. and Chung, H. H., " Simultaneous oxidation of EDTA and reduction of metal ions in mixed Cu(II)/Fe(III)-EDTA system by TiO₂ photocatalysis ", Chemosphere, Vol.64, pp.432-436, 2006. 32. Papadama, T., Nikolaos, P., Xekoukoulakis, Poulios, I. and Mantzavinos, D., " Photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous TiO₂ suspensions ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.186, pp.308 – 315, 2007. 33. Parida, K.M., Sahu , N., " Visible light induced photocatalytic activity of rare earth titania nanocomposites ", Journal of Molecular Catalysis A: Chemical, Vol.287, pp.151 – 158, 2008. 34. Ranjit, K. T., Varadarajan, T. K. and Viswanathan, B., " Photocatalytic reduction of nitrite and nitrate ions on Ru / TiO₂ catalysts ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.89, pp.67-68, 1995a. 35. Ranjit, K. T., Krishnamoorthy, R., Varadarajan, T. K. and Viswanathan, B., " Photocatalytic reduction of nitrite on CdS ", Journal of Photochemistry and PhotobiologyA: Chemistry, Vol.86, pp.185-189, 1995b. 36. Ranjit, K. T., Varadarajan, T. K. and Viswanathan, B., " Photocatalytic reduction of dinitrogen to ammonia over noble-metal-loaded TiO₂ ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.96, pp.181-185, 1996. 37. Ranjit K. T. and Viswanathan, B., " Photocatalytic reduction of nitrite and nitrate ions to ammonia on M / TiO₂ catalysts ", Journal of Photochemistry and Photobiology A:Chemistry, Vol.108, pp. 73-78, 1997a. 38. Ranjit K. T. and Viswanathan, B., " Photocatalytic reduction of nitrite and nitrate ions over doped TiO₂ catalysts ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.107, pp.215-220, 1997b. 39. Rengaraj, S. and Li, X. Z., " Enhanced photocatalytic reduction reaction over Bi3+ – TiO₂ nanoparticles in presence of formic acid as a hole scavenger ", Chemosphere, Vol.66, pp.930 – 938, 2007. 40. Subrahmanyam M., Kaneco S. and Alonso-Vante N., " A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C1 - C3 selectivity ", Applied Catalysis B: Environmental, V.23, pp.169-174, 1999. 41. Shifu, C. and Gengyu, C., " Study on the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos ", Chemosphere, Vol.60, pp.1308-1315, 2005. 42. Tawkaew, S., Tawkaew, Fujishiro, Y., Sku,Y. and Tsugio S., " Synthesis of cadmium sulfide pillared layered compounds and photocatalytic reduction of nitrate under visible light irradiation ", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol.179, pp.139 – 144, 2001. 43. Tan T., Beydoun, D. and Amal, R., " Effects of organic hole scavengers on the photocatalytic reduction of selenium anions ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.159, pp. 273 – 280, 2003. 44. Tuprakay, S. and Liengcharernsit, W., " Lifetime and regeneration of immobilized titania for photocatalytic removal of aqueous hexavalent chromium ", Jouurnal of Hazardous Materials, Vol.124, pp.53-58, 2005. 45. Wang, C.F., Yu, C.T., Lin, B.H., Lee, J.H., " Synthesis and characterization of TiO₂/BaF₂/ceramic radio-sensitive photocatalyst ", Journal of Photochemistry and Photobiology A: Chemistry, Vol.182 pp.93 – 98, 2006. 46.

Witońska, I., Karski, S., Rogowski, J., Krawczyk, N., "The influence of interaction between palladium and indium on the activity of Pd – In/Al₂O₃ catalysts in reduction of nitrates and nitrites", Journal of Molecular Catalysis A: Chemical, Vol.287, pp.87 – 94, 2008. 47. Xie, B., Zhang, H., Cai, P., Qiu, R. and Xiong, Y., "Simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol over monoclinic BiVO₄ under visible light irradiation", Chemosphere, Vol. 63, pp.956-963, 2006. 48. Yu, J., Zhao X. and Zhao, Q., Materials Chemistry and Physics, Vol.69, pp.25-29, 2001. 49. Yahaya, A. H., Gondal, M. A. and Hameed, A., "Selective laser enhanced photocatalytic conversion of CO₂ into methanol", Chemical Physics Letters, Vol.400, pp.206-212, 2004. 50. Young Ku., Wan-Hui Lee. and Wen-Yu Wang., "hotocatalytic reduction of carbonate in aqueous solution by UV/TiO₂ process", Journal of Molecular Catalysis A: Chemical V.212, 191 – 196, 2004. 51. Zhang, F., Zhang, Jin, R., Chen, J., Shao, C., Gao, W., Li, L. and Guan, N., "High photocatalytic activity and selectivity for nitrogen in nitrate reduction on Ag/TiO₂ catalyst with fine silver clusters", Journal of Catalysis, Vol.232, pp.424 – 431, 2005.