

Ternary Wide Band Gap p-Block Metal Semiconductor ZnGa₂O₄ for Photocatalytic Benzene Degradation

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Introduction

Benzene is a widespread environmental pollutant. Although TiO₂-based photocatalytic oxidation (PCO) has been established to be one of the most promising technologies for the environment remediation, PCO meets with limited success in the treatment of aromatic compounds like benzene due to the deactivation of TiO₂ resulted from the accumulation of the stable reaction intermediates on the surface. The development of new photocatalysts with high performance for benzene degradation is indispensable.

Our recent studies have shown that some wide band gap p-block metal semiconductors like Ga₂O₃, In(OH)₃, InOOH and Sr₂Sb₂O₇ [1] show high activity and stability in the photocatalytic degradation of benzene. The high photocatalytic performance observed over these wide band gap p-block metal semiconductors is related to their peculiar electronic structure. However, the already known wide band gap p-block metal semiconductor photocatalysts are limited. Besides this, except the common characteristics like wide band gap and the dispersive conduction band, other factors influencing their photocatalytic activity remain largely unclear. To study these influencing factors, more wide-band gap p-block metal semiconductors, especially those ternary ones, due to their diversified crystallographic and electronic structure, and their photocatalytic activity should be investigated.

Herein we reported the preparation of nanocrystalline ZnGa₂O₄ via a co-precipitation method and the study of its photocatalytic activity for benzene degradation. The as-prepared ZnGa₂O₄ showed superior photocatalytic activity and stability for benzene degradation to commercial TiO₂. However, its activity is lower as compared to another ternary wide band gap p-block metal semiconductor photocatalyst Sr₂Sb₂O₇. The difference of the photocatalytic activity between ZnGa₂O₄ and Sr₂Sb₂O₇ can be well explained by their different geometric structures.

Materials and Methods

Nanocrystalline ZnGa₂O₄ was prepared by a co-precipitation method. Aqueous solutions of Zn(NO₃)₂·6H₂O and Ga(NO₃)₃·xH₂O were mixed in the molar ratio of 1:2. Under vigorous stirring, ammonia solutions were dropped simultaneously into the mixed nitrate solutions until the pH value was in the range of 7~8. Then the precipitate slurry was thoroughly stirred. The precipitate was separated, washed with distilled water and absolute ethanol for several times. The precipitation obtained was dried in air at 80 °C, and then ground and sintered at 600 °C for 5 h in air.

The photocatalytic degradation of benzene was conducted in a tubular quartz micro-reactor operating in a continuous-flow mode under 254 nm UV illuminations. The initial benzene concentration was 220 ppm.

Results and Discussion

The XRD of the as-prepared sample indicates the formation of the pure phase of ZnGa₂O₄ (Figure 1). Figure 2 shows the conversion of benzene and the amount of the produced CO₂ over the as-prepared ZnGa₂O₄ and P25 as a function of illumination time. The benzene conversion over ZnGa₂O₄ was about 12.0 % and more than 100 ppm of CO₂ was produced, which corresponds to a high mineralization ratio of about 63 %. The high conversion and mineralization ratio can be maintained for more than 20 h.

Although the photocatalytic performance for benzene degradation over ZnGa₂O₄ (12%) is superior to that over P25, it is lower than that of Sr₂Sb₂O₇ (24%). The order of the photocatalytic activity between Sr₂Sb₂O₇ and ZnGa₂O₄ can not be explained by their BET specific surface area (36.7 m²·g⁻¹ for ZnGa₂O₄ vs. 24.8 m²·g⁻¹ for Sr₂Sb₂O₇) or their band gap energies (4.7 eV for ZnGa₂O₄ and 4.2 eV for Sr₂Sb₂O₇). The crystallographic structure analyses of ZnGa₂O₄ and Sr₂Sb₂O₇ reveal that the geometric structure of the interior polyhedra in these two semiconductors is different. In ZnGa₂O₄, the GaO₆ octahedron is normal without any distortion. However in Sr₂Sb₂O₇, one type of SbO₆ is an elongated octahedron with two longer Sb–O bonds compared to the remaining four bonds with the same bond length, while the other type of SbO₆ is a compressed octahedron with two shorter Sb–O bonds. This difference in the geometric structure may explain the different photocatalytic activity between Sr₂Sb₂O₇ and ZnGa₂O₄. This result indicates that the distortion of the interior polyhedra is probably favorable for the photocatalytic activity.

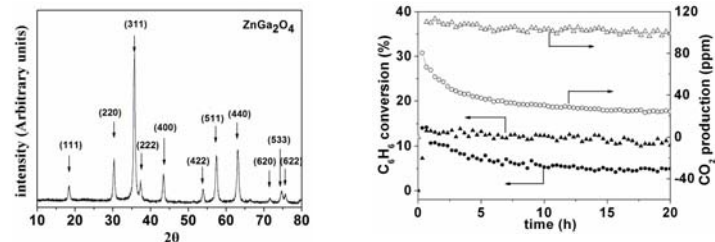


Figure 1 XRD patterns of the nanocrystalline ZnGa₂O₄

Figure 2 The conversion of C₆H₆ and the amount of produced CO₂ over the nanocrystalline ZnGa₂O₄ as a function of reaction time, with TiO₂ (P25) as references. (▲) (●) the conversion of C₆H₆ over the ZnGa₂O₄ and TiO₂ respectively, (Δ) (○) the amount of produced CO₂ over the ZnGa₂O₄ and TiO₂ respectively.

Significance

This study reveals that the crystallographic structure can influence the photocatalytic activity of these wide band gap p-block semiconductors. This study gives some new insights in the development of new ternary wide band gap p-block semiconductor photocatalysts for benzene degradation.

References

1. Xue, H.; Li, Z. H.; Wu, L.; Ding, Z. X.; Wang, X. X.; Fu, X. Z. *J. Phys. Chem. C* (2008), 112, 5850.