



## Photodegradation of Phenol Using $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Supported Nano-ZnO

YONGHONG ZHAO\*, RUJIN KANG, ZHIPING DU and HAIBO DONG

Nanotechnology Applied Research Center of Shanxi Province, China Research Institute of Daily Chemical Industry, Taiyuan 030001, P.R. China

\*Corresponding author: Tel/Fax: +86 351 2027036; E-mail: zyh-327@163.com

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The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO was prepared by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with zinc-ammonia solution. The as-prepared samples were analyzed by XRD, SEM and BET. Phenol was used as a probe to evaluate the photocatalytic activity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO. The results indicate that ZnO was successfully adsorbed on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a particle size of 7.4 nm. The surface area and pore volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> itself and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO were 150.82, 106.32 m<sup>2</sup>/g and 0.67, 0.47 cm<sup>3</sup>/g, respectively. The photodegradation rates showed that the photocatalytic performance of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites was better than that of ZnO. The influence of dosage of the ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites and initial concentration of phenol on the photocatalytic performance were investigated. The results showed that the optimum ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites dosage was 0.4 g for 100 mL phenol solution and the degradation rate was decreasing with the initial concentration of phenol enhancement. Besides, the repeatability of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites was also investigated in this work.

**Key Words:** ZnO,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Carrier, Photodegradation, Phenol.

### INTRODUCTION

As important chemical materials, phenol and its derivatives are widely present in a variety of wastewaters from various different industries, such as paper mills, oil refining, coking, *etc.*<sup>1</sup>. In sewage, the biodegradation of phenolic compounds are not possible with leading to serious environmental problems and harmful for health due to their carcinogenic, teratogenic and mutagenic properties<sup>2</sup>. Efforts have been made to develop new waste treatment techniques including granular activated carbon adsorption, ozonation and photodegradation<sup>3</sup>. Among them, photodegradation has been attracted great attention for its high efficiency, commercial availability and high chemical stability in the degradation of various environmental pollutants over conventional methods of waste treatment<sup>4</sup>. Photodegradation of phenol solution has been performed over various photocatalysts, such as TiO<sub>2</sub>, ZnO and SnO<sub>2</sub> *etc.*<sup>5-7</sup>.

Heterogeneous photocatalysis with semiconductors, such as TiO<sub>2</sub> and ZnO has been extensively investigated as a promising method for pollutants removal. The mechanism of photocatalysis is that when the semiconductor particles are illuminated with light having an energy equal to or higher than the band gap energy between its valence and conduction bands, an electron (e<sup>-</sup>) promotes from the valence band to the conduction band due to photoexcitation, thus generating a hole (h<sup>+</sup>) in the valence band<sup>8</sup>. The electron/hole pairs can either

recombine or can interact separately with other molecules. The recombination of the electrons and the holes should be prevented as much as possible in order to retain photocatalysis. In aerated aqueous systems, the photogenerated h<sup>+</sup> oxidize H<sub>2</sub>O or HO<sup>-</sup> at the surface of the semiconductor to produce HO<sup>•</sup> radicals as a strong oxidizing agent which could oxidize most organic pollutants up to CO<sub>2</sub>, H<sub>2</sub>O and/or the mineral end-products<sup>9</sup>.

ZnO is a highly fascinating candidate as an alternative to TiO<sub>2</sub>, which has been found to be the most active photocatalyst, owing to their similar chemical-physical characteristics and photodegradation mechanisms<sup>10-12</sup>. In addition, ZnO is available at low cost and shows better performance compared to that of TiO<sub>2</sub> in the degradation of several organic contaminants in both acidic and basic medium<sup>13-15</sup>. In many applications, ZnO has been used in the form of fine powders suspended in water, so-called slurry type. Due to large surface area of the dispersion of nano-sized particles, the slurry type exhibits excellent photocatalysis. However, this way also has some limitations including low light-utilization efficiency caused by light absorption and scattering in aqueous suspension. Further more, filtration or centrifugal separation are required to separate the catalyst from water after the photocatalytic process. Therefore, much work has been done to improve photodegradation of nano-ZnO by loading the powders on substrate materials<sup>16</sup>.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> with porosity, large surface area and thermal stability has been widely used as catalyst support<sup>17</sup>. Here the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO was prepared by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with zinc-ammonia solution. Phenol was used as a probe to evaluate the photocatalytic activity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO.

## EXPERIMENTAL

Commercial zinc oxide (ZnO) was purchased from Huludao Zinc Industry Co. Ltd. Ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) was purchased from Xinji Tianjia Chemical Co. Ammonia was purchased from Taiyuan Chemical Reagent Factory. Phenol was purchased from Tianxin Fine Chemical Development Center. Absolute ethanol was purchased from Beijing Chemical Co.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was produced by China Research Institute of Daily Chemical Industry. All materials were used without further purification.

### Methods

**Preparation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO:** Firstly, a zinc-ammonia solution were prepared by dissolving commercial ZnO and NH<sub>4</sub>HCO<sub>3</sub> (molar ratio: 1:1.4:3) into ammonia at room temperature with vigorous stir to get a light blue solution. Then, 0.5 g  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (60-80 mesh) was put into 6.3 mL above zinc-ammonia solution and heated to 90 °C for 4 h to prepare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO. The sample was filtrated and washed with deionized water then absolute ethanol for 3 times, respectively. The as-prepared nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was dried and calcined at 300 °C for 2 h.

**Characterization of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:** To determine the composition of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> X-ray diffraction (XRD) was carried out at room temperature using a Rigaku D/MAX-RB diffractometer with CuK $\alpha$ . A continuous scan mode was used to collect the diffraction with a speed of 6° (2 $\theta$ )/min between 20 and 80°. The accelerating voltage and the applied current were 40 kV and 100 mA, respectively. Scanning electron microscope (SEM, JSM-35C) was employed to detect the surface morphology of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The surface area was obtained from nitrogen adsorption isotherm by the Brunauer-Emmett-Teller (BET) method using in a Micromeritics ASAP2010 sorptometer at 77 K.

**Evaluation of photodegradation of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:** Photocatalytic activity of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was evaluated using phenol as a probe. A 500W high-pressure xenon lamp (> 380 nm) was used as the irradiation source. Aqueous suspensions (100 mL) containing the phenol (10 mg/L) and the photocatalysts were added in a 200 mL Pyrex columned photo-reactor followed by 4 h mechanical stirring and irradiation. After an appropriate irradiation period, 5 mL the phenol solution were taken and analyzed with UV-VIS spectrophotometer (UV-1600, Beijing Rayleigh Analytical Instrument Corp.). The concentration of phenol (C) was in proportion to the light absorbance (A) at 269 nm according to Beer-Larrant law<sup>18</sup> and so the photodegradation rate (P) could be calculated as the following equation.

$$P = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

## RESULTS AND DISCUSSION

**Structure characterization of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:** The XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier and ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 1. Obvious diffraction peaks at  $2\theta = 31.8, 34.4, 36.3, 47.5, 56.6$  and  $62.9^\circ$  were observed corresponding to the (100), (002), (101), (102), (110) and (103) crystal faces of ZnO, respectively. Some of the diffraction peaks are overlapped with these of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> partially due to the close location between them. The crystal sizes ( $d = 7.4$  nm) of the nano-particles could be estimated by Debye-Scherrer equation,  $d = k\lambda/(\beta \cos \theta)$ , according to the peak width of  $56.6^\circ$  for ZnO in XRD pattern<sup>19</sup>.

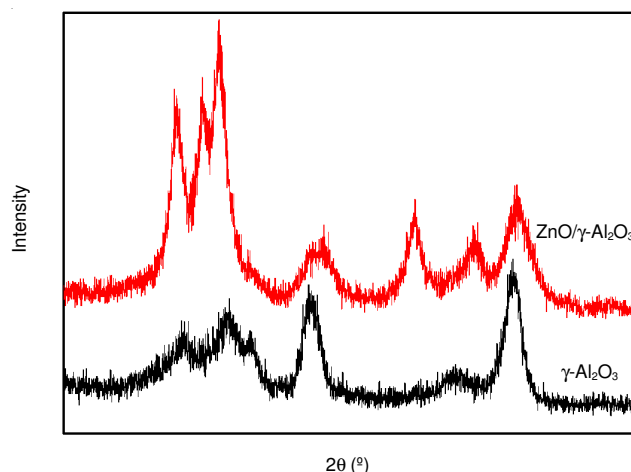


Fig. 1. XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites

**Surface morphology of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:** Fig. 2 shows the surface micrograph of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites. It can be seen that the surface of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier were rough and porous, but the surface of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> looked much smooth. The result indicates that ZnO has been adsorbed on the surface of the carrier successfully.

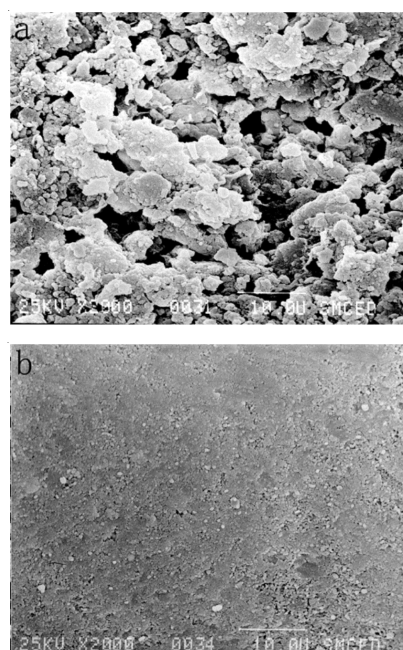


Fig. 2. Surface micrograph of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites

**Surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:** The surface area and pore volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were obtained from BET nitrogen adsorption isotherm measured, which were 150.82, 106.32 m<sup>2</sup>/g and 0.67, 0.47 cm<sup>3</sup>/g, respectively. Clearly, both the specific surface areas and pore volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were shrunk after ZnO adsorption, *i.e.*, the surface and pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were covered by ZnO partially. The results might imply that nano-ZnO aggregated on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, but not get into the pores of the carrier.

**Photocatalytic activity:** Fig. 3 gives the time evolution of degradation rate of phenol in an aqueous system. The residual phenol was measured as mentioned earlier. It was found that degradation rate of phenol was only less than 5 % in the absence of the UV irradiation and was *ca.* 15 % without any photocatalyst. However, under UV irradiation the photocatalytic activity of ZnO was obviously high. It may suggest that the photocatalyst made photodegradation of organic pollutants under light irradiation. Surface adsorption was less important in the process and the degradation of phenol could hardly be catalyzed by ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> without UV light irradiation. After 4 h UV irradiation, the photodegradation rate of phenol could reach 87.6 % using ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, then only 74.5 % using ZnO alone. This phenomenon was attributed to the synergistic effect between ZnO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>20</sup>.

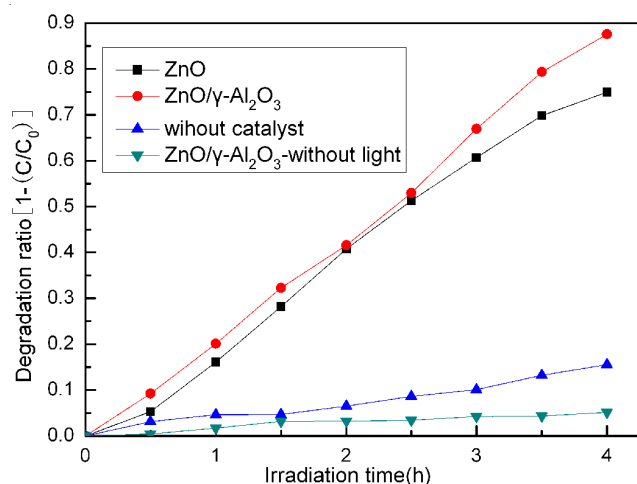


Fig. 3. Degradation activity vs. time curves for the degradation of phenol solution with or without photocatalyst

Fig. 4 shows the degradation rate of phenol with UV irradiation time in the presence of different dosage ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It is clear that the photocatalytic activity of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was related to the dosage of the catalyst in certain extent. When the dosage of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was up to 4 g/L, the highest photodegradation rate of phenol could be obtained in the experiments. After the dosage of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rose to 5 g/L, the photodegradation rate decreased. It indicates that there is an optimal concentration for ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to photocatalyze the degradation of phenol. This might cause by the so-called shielding effect at higher concentration of catalyst, because excessive ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> resulted in cloudy suspension, which may reduce the intensity of the UV irradiation. Similar behaviours were also observed in ZnO catalyst without  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier<sup>21</sup>.

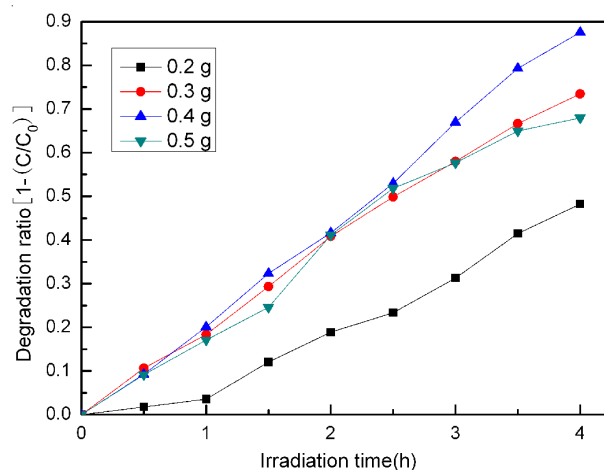


Fig. 4. Influence of the dosage of nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites on the degradation rate of phenol solution

Fig. 5 represents the time evolution of photodegradation rate with different initial concentration of phenol in the presence of 4 g/L ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It can be found that in a diluted system (10 mg/L), almost 87.6 % phenol could be degraded after 4 h irradiation. When the initial concentration of phenol increased to 20 mg/L, the degradation rate dropped sharply to less than 50 %. The photodegradation rate decreased further with the increase of initial concentration of phenol. At higher phenol initial concentration, the adsorption of phenol molecules on the catalyst surface hindered competitive adsorption of OH<sup>-</sup> ions, thus, lowering the formation rate of hydroxyl radicals, which thereby led to the decrease of the photodegradation activity of phenol<sup>22</sup>.

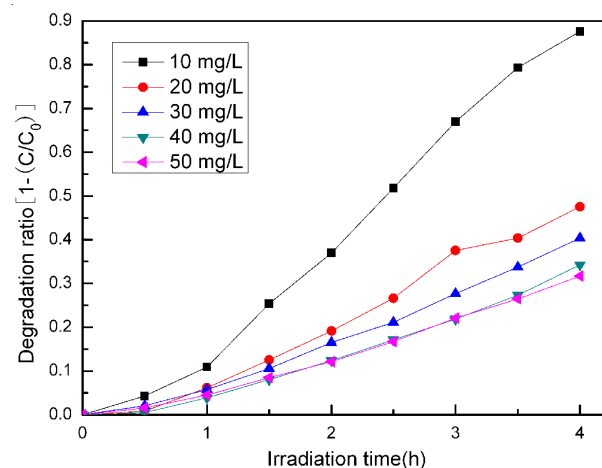


Fig. 5. Effect of initial phenol concentration on the photodegradation activity

The reusability of the photocatalyst is an important parameter to assess the catalyst practicability. Yassitepe *et al.*<sup>23</sup> have carried out the related experiments on the ZnO for degradation of reactive red 180 (RR 180). The time evolution of the phenol degradation rate using the as-prepared ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as catalyst in 3 times reusing was shown in Fig. 6. The recycled photocatalyst was treated with heating at 110 °C for 2 h at every cycle. It can be seen that the degradation rate decreased from 87.6-67.6 % after three cycles, diminishing *ca.* 20 %. This phenomenon may be explained by partial loss of ZnO

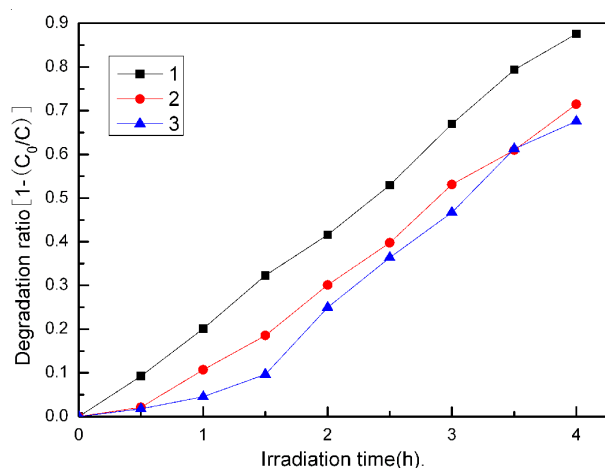


Fig. 6. Effect of recycle time on the degradation rate of phenol. (experimental condition: nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites dosage: 0.4 g; phenol concentration: 10 mg/L)

from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier and photocatalyst deactivation<sup>24</sup>. The degradation intermediate of phenol may also adsorb on the surfaces of the photocatalyst resulting in a further deactivation. The heat treatment may also induce some catalyst aggregation after several recycles bringing some decrease of the surface area and finally leading to further decrease of photocatalytic activity<sup>25</sup>.

### Conclusion

The method of impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with zinc-ammonia solution could be used to prepare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported nano-ZnO. The photocatalytic activity of the obtained nano-ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was better than this of nano-ZnO alone for the degradation of phenol. Initial phenol concentration and the dosage of ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> could affect the degradation process. The as-prepared ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited a reasonable reusability and after 3 cycle the degradation rate of phenol could also reach 67.6 %.

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