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# Fabricate and characterization of Ag/$BaAl_2O_4$ and its photocatalytic performance towards oxidation of gaseous toluene studied by FTIR spectroscopy

Zhengru Zhu [*], Feiya Liu, Wei Zhang

*Research Center of Hydrology and Water Source, School of City and Environmental Science, Liaoning Normal University, Dalian 116029, China*

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ABSTRACT

Porous and rod-shaped nanostructure of $BaAl_2O_4$ was successfully synthesized by using a simple hydrothermal method. Ag-doped $BaAl_2O_4$ catalyst based on the porous $BaAl_2O_4$ was prepared by incipient wetness impregnation strategy, which showed excellent photoelectric property and catalytic activity. The structural properties of the samples were systematically investigated by XRD, BET, SEM, EDX, TEM, DRS, XPS and FT-IR techniques. The results revealed that the prepared Ag/$BaAl_2O_4$ nanorods were more active than $BaAl_2O_4$ and commercial $TiO_2$ in photocatalytic oxidation of gaseous toluene. The photodegradation ratio of toluene over Ag/$BaAl_2O_4$ reaches to 88%. The toluene was not complete degradation over these catalysts which only partial oxidations were achieved under UV illumination. The weakly adsorbed benzaldehyde is formed during photocatalysis. Hydroxyl groups on the surface of the catalyst are able to react with benzaldehyde which played a key role in the photocatalytic process.

## 1. Introduction

Volatile organic compounds (VOCs) released into the atmosphere as a consequence of man-made emission undergo a complex physical–chemical transformations before they are decomposed or deposited to the earth's surface [1]. VOCs are pollutants harmful to humans, and the control of VOCs emission can be achieved at low temperatures by means of catalytic combustion, the efficiency of which is determined by the activity and stability of the adopted catalysts [2–5]. Particularly, toluene is a major air pollutant indoor and industrial which is a very noxious organic compound. Many strategies have been identified to reduce its presence in the environment.

Several advanced oxidation technologies have been studied for toluene removal, among which the photocatalytic oxidation over $TiO_2$ appears to be mostly attractive [6,7]. However, the catalyst is often rapidly deactivated, especially during aromatics oxidation, due to accumulation of less-reactive by-products on the photocatalyst surface [6]. Numerous supported noble metals and alkaline-earth metal have been investigated for the catalytic combustion of VOCs [8,9]. The notable advantages of supported noble metal catalysts are relatively high activity, mild process conditions, easy separation, and better handling properties. Ag species significantly improve the activity, selectivity, recycling, and reproducibility of Ag catalyst systems, so loading noble metal Ag can be a feasible way to enhance catalytic activities of the semiconductors. But the amounts of loading metal should be controlled in a suitable range. The excessive noble metals possibly become the recombination centre of electronic and the hole, thus make the activities of the catalysts be decreased. Although the catalysts based on precious metals are highly active at relatively low temperatures, their applications are limited due to expensive cost and problems related to sintering and volatility of the noble metals. Among the oxides of alkaline-earth metals, spinel-type oxides ($AB_2O_4$) are promising catalysts for the complete oxidation of hydrocarbons and oxygenates. Wrzyszcz et al. [10] and Zawadzki et al. [11] have reported Pt/$ZnAl_2O_4$ and Pd/$ZnAl_2O_4$ and then discussed the interaction between the metal and the support. Jackson and Shaw [12] studied the properties of Rh/$ZnAl_2O_4$ is more stable than $Al_2O_3$/$ZnAl_2O_4$. Li et al. [13] and Okal and Zawadzki [14] have reported the photocatalytic activities about $TiO_2$/$BaAl_2O_4$ and Ru/$ZnAl_2O_4$ nanoparticles. Ragupathi et al. [15] have reported the $ZnAl_2O_4$ which prepared by the microwave method showed higher catalytic activity for the oxidation of benzyl alcohol. We have also demonstrated that Ag/$NiFe_2O_4$ nanoparticles could greatly increase toluene photooxidation efficiency and stability [16].

The metal oxide compounds with one-dimension nanorods or nanostructures, especially their characteristics such as catalytic activity, the selectivity, the electrical conductivity or the photonic

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[*] Corresponding author. Tel.: +86 411 8215 8364; fax: +86 411 8215 8542.
*E-mail address:* zhengruzhu@gmail.com (Z. Zhu).

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efficiency and so on, usually have the close connection with the specific surface areas and the particle sizes. $BaAl_2O_4$, which belongs to the family of stuffed tridymites, is a high-melting-point material with good dielectric, pyroelectric, and hydraulic-hardening properties. It has been studied for coating and refractory cement applications [17,18]. $BaAl_2O_4$ is also notable for its good luminescent performance [19]. However, as far as we know, the catalytic performance and photodegradation capacity of $BaAl_2O_4$ towards toluene for has not been still reported.

In the present work, a $BaAl_2O_4$ sample with porous and rod-shaped was obtained via a simple and economic hydrothermal treatment. And then noble metal Ag loaded on the $BaAl_2O_4$ (pH 6) by a traditional wetness impregnation method, which formed Ag/$BaAl_2O_4$ nanorods. After systematic characterization of the nanorods and surface structures, $BaAl_2O_4$, Ag/$BaAl_2O_4$ nanorods and nanostructured $TiO_2$ samples are investigated for the photocatalytic activity and the reaction mechanism of over the photooxidation of gaseous toluene by using an *in-situ* FTIR cell under UV irradiation.

## 2. Experimental

### 2.1. Preparation of catalysts

Both precursors of $Ba(NO_3)_2·5H_2O$ and $Al(NO_3)_3·9H_2O$ were used in this work to study the formation of nanocrystalline $BaAl_2O_4$ through hydrothermal process. The molar ratio of Ba/Al is fixed at 1:2. Desired amounts of $NH_3·H_2O$ were added to the mixture (100 mL) to adjust pH value. When the pH value is 6, the mixture was put into a Teflon-lined stainless steel autoclave of 120 mL in capacity at 200 °C for 20 h. Then, the system was allowed to natural cooling to room temperature. The precipitate was then washed twice with deionized water and ethanol, respectively. After that, the precipitate was dried overnight at 80 °C and the residual water was further removed by heating at 750 °C for 5 h. Then white $BaAl_2O_4$ sample was obtained.

The catalyst of porous $BaAl_2O_4$ supported Ag was prepared by a conventional wet impregnation route [20]. $AgNO_3$ solution was used as the precursor. The Ag loading was 1% wt. After evaporation, the catalyst was then dried at 100 °C for 12 h and calcined at 400 °C in air for 6 h followed by slow cooling under air atmosphere. Then white Ag/$BaAl_2O_4$ powders were obtained. All the materials were reagent grade and used without further purification. Deionized water was used as a solvent.

### 2.2. Characterizations

The phase compositions and structures of the $BaAl_2O_4$ and Ag/$BaAl_2O_4$ samples prepared were determined by X-ray diffraction (XRD, RIGAKU, Dmax22000) with Cu Kα radiation ($\lambda = 0.15418$ nm) over the 2θ range of 20–75° with a step of 0.02°.

The morphology of these samples was investigated by scanning electronic microscopy (SEM) with a JSM-6700 LV electron microscope operating at 5.0 kV and transmission electron microscope (TEM, FEI Tecnai G220).

Surface area of these samples was determined by Brunauer-Emmet-Teller (BET), $N_2$ gas adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP-2000 equipment. Sample was previously degassed at 400 °C. Pore size distributions were calculated by the BJH model.

Ultraviolet–visible diffuse reflectance spectra between 200 and 800 nm (DRS, Shamazu-UV-240) of the products were collected.

Fourier transform infrared (FTIR, Bruker Vertex 70) spectra were recorded in the range 4000–400 $cm^{-1}$ with 4 $cm^{-1}$ resolution.

XPS data were recorded using a PerkinElmer PHI 5600 electron spectrometer by acrochromatic Al Kα radiation (1486.6 eV) with $Ar^+$ sputtering to remove the surface layer of the samples.

The photocatalytic activity (PCA) was measured to the concentration change of toluene using a gas chromatography (Aligent 7890A, USA) and an *in-situ* FT-IR spectroscopy (BRUKER VERTEX 70 Optics).

### 2.3. Photocatalytic experiments of the $BaAl_2O_4$, Ag/$BaAl_2O_4$ and commercial P25 catalysts

The photocatalytic experiments were carried out in an apparatus using a self-made *in-situ* IR quartz photoreaction cell. The photoreactor operating in the gas–solid regime was a cylindrical shaped batch type quartz photoreactor. The cell had a path length of 10 cm and tubular diameter of 4 cm. Both ends were "capped" by IR-transparent NaCl crystal windows. Approximately 0.1 g of the samples were pressed into a self-supported disk of 13 mm in diameter. The disk was mounted inside the sample holder (its diameter was about 13 mm) located at the center of the cell and allowed UV illumination. The sample holder was tilted by an angle of 30 degree with respect to the IR path. The distance between the UV lamp (15 W, Philips) and sample was about 15 cm. The wavelength of UV lamp is 365 nm, the light intensity at the

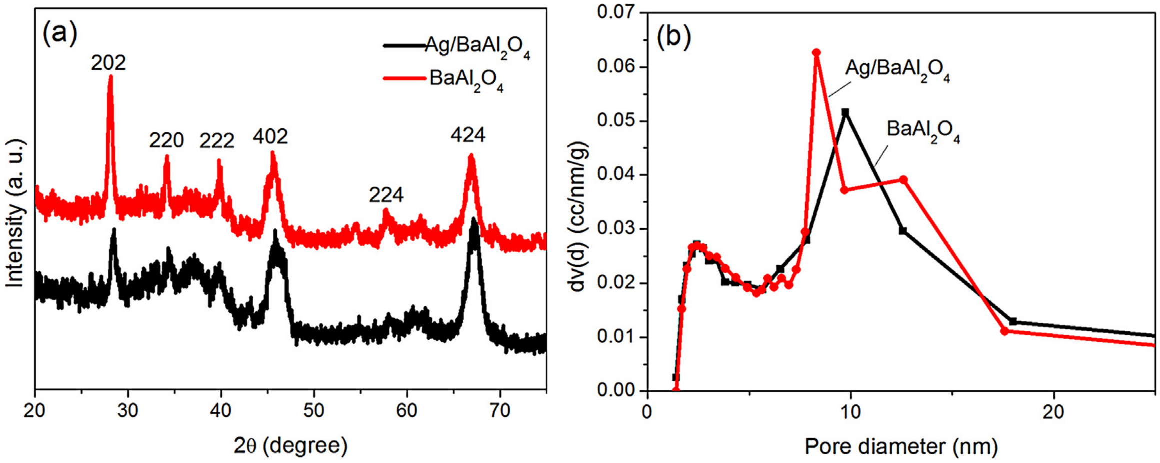

**Fig. 1.** The XRD patterns of the $BaAl_2O_4$ and Ag/$BaAl_2O_4$ samples (a) and BJH desorption size distributions of the $BaAl_2O_4$ and Ag/$BaAl_2O_4$ samples (b).