Characterization, Degradation, and Reaction Pathways of Indoor Toluene over Visible-light-driven S, Zn Co-doped TiO$_2$

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**Abstract.** Sulfur and Zinc co-doped TiO$_2$ prepared by a sol-gel method to degrade toluene under a fluorescent lamp was investigated. The results indicate that S,Zn co-doped TiO$_2$ photocatalysts are mainly nano-size with an anatase phase structure. The degradation reactions of toluene were performed under various operation conditions. The results show that the toluene conversion increases with increasing toluene concentration and decreasing relative humidity. Based on the results of activity test, S$_{0.05}$Zn$_{0.001}$/TiO$_2$ was chosen for further studies. The main oxidation products of toluene photodegradation are CO$_2$, H$_2$O, benzyl alcohol, acetone, butadiene and acetic acid. Two possible mechanisms have been developed for photodegradation of toluene in a dry and a humid environment.

**1. Introduction**

Indoor air pollution has received increasing attention in recent years since people spend almost 90 percent of their time indoors [1]. Volatile organic compounds, which are usually emitted from construction materials, household products, and office furnishings, are the main indoor air pollutants [2]. Toluene, as one of the most predominant VOCs, is widely applied to rubber, paint, ceiling, disinfectant, tackiness agent, and chemical reactants. Toluene has high toxicity, carcinogenicity and long persistence in the indoor environment. Therefore, the removal of toluene is an important task for the indoor air quality. Photocatalytic oxidation (PCO) using TiO$_2$ has recently received considerable attention for VOCs removal due to its cost-effectiveness, non-toxicity, fast oxidation rate, and chemical stability [3]. This study was conducted under various operating conditions. The characteristics of photocatalysts, photodegradation of toluene, and pathway of toluene photooxidation have been investigated under a fluorescent lamp.

**2. Materials and methods**

2.1. Photocatalyst preparation

Sulfur and Zinc co-doped TiO$_2$ with various mole ratios were prepared by a sol-gel method. In the preparation process of Ti-precursor sol, titanium tetra-isopropoxide (TTIP) (30 mL) was mixed with absolute ethanol (45 mL). Then the mixture was slowly added into deionized water (360 mL) at room temperature during continuous stirring. After mixture was stirred vigorously at room temperature for 30 min, 1.2 ml of HNO$_3$ (65 wt%) was slowly added dropwise into the mixture, which was further
stirred until the gel formed. The final solution was heated on a hot plate set at 70°C and constantly stirred until the liquid fully evaporated. Finally, the residual was calcined at 500°C for 3 h in air. On the basis of the previous study [3], the S/Ti molar ratio was chosen as 0.05 and the Zn/Ti molar ratio was y. In the preparation of S\textsubscript{0.05}Zn\textsubscript{y}/TiO\textsubscript{2}, the pre-determined amounts of 0.37 g thiourea (CH\textsubscript{4}N\textsubscript{2}S) and the pre-determined amounts of zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O) was dissolved in 360 mL de-ionized water first, and the subsequent processes were the same as the method described above.

2.2. Photocatalyst characterization
The XRD patterns were obtained on a Rigaku X-ray diffraction (Model D/MAS IIIV, Rigaku) using Cu Kα radiation to determine the major crystal phases. The crystallite sizes of the photo-catalysts were calculated by using Scherrer’s formula [4].

2.3. Photocatalytic activity measurements
The reaction gas of toluene was generated using a programmable syringe pump. The reaction gas of toluene was mixed with cylinder air and water vapor according to target toluene concentrations, ranged from 0.5 to 2 ppm. The reaction gases before and after the experiments were analyzed with a gas chromatography (GC)/flame ionization detector and fitted with a DB-624 capillary column. A 10W fluorescent lamp (FL-10D, emission range between 360 and 580nm with \( \lambda_{\text{max}} = 436 \) nm) was used as the photon source and the light intensity was 2.5 mW cm\(^{-2}\). The by-products and products were analyzed using an on-line FTIR spectrophotometer (Model Spectrum One, Perkin Elmer), operating in the spectral range of 4,000 to 700 cm\(^{-1}\).

3. Results and discussion
3.1. XRD analysis
The crystal phases, average crystalline sizes, and lattice parameters of various photocatalysts are listed in Table 1. The crystal phase of bare TiO\textsubscript{2} and co-doped TiO\textsubscript{2} are all anatase phases checked from JCPDS Card No. 21-1272. The crystallite size of bare TiO\textsubscript{2} is about 16 nm, and those of TiO\textsubscript{2} co-doped with sulfur or zinc are about 11 nm. The doping reduces the grain size, which is attributed to the lattice distortion caused by the incorporation of S and Zn into the TiO\textsubscript{2} matrix. The phenomena can be demonstrated from the change in lattice parameter of TiO\textsubscript{2}. The results show the occurrence of a slight lattice distortion in the crystal structure. For S\textsubscript{0.05}/TiO\textsubscript{2}, the ionic radius of S\textsuperscript{6+} (0.12 Å) is smaller compared to that of Ti\textsuperscript{4+} (0.68 Å), which can substitute Ti\textsuperscript{4+} ions in the TiO\textsubscript{2} crystal lattice, and leads to the formation of Ti–O–S bond. The SZ co-doped TiO\textsubscript{2}, Zn\textsuperscript{2+} ions do not enter into crystal lattice of TiO\textsubscript{2} because ionic radius of Zn\textsuperscript{2+} (0.74 Å) is larger than Ti\textsuperscript{3+} (0.68 Å) in the TiO\textsubscript{2} structure [5]. Therefore, Zn\textsuperscript{2+} ions are dispersed on the surface of the S/TiO\textsubscript{2} particles in the form of ZnO clusters during the calcination process.

| Sample                | Crystal phase | Crystallite size | Lattice parameter |
|-----------------------|---------------|------------------|------------------|
|                       | Anatase (%)   | d\textsubscript{A} (nm) | a (Å) | c (Å) | c/a    |
| TiO\textsubscript{2}  | 100           | 16.6             | 3.777            | 9.517 | 2.520  |
| S\textsubscript{0.05}/TiO\textsubscript{2} | 100           | 11.9             | 3.783            | 9.492 | 2.509  |
| S\textsubscript{0.05}Zn\textsubscript{0.00}/TiO\textsubscript{2} | 100           | 11.7             | 3.787            | 9.483 | 2.504  |
| S\textsubscript{0.05}Zn\textsubscript{0.01}/TiO\textsubscript{2} | 100           | 11.8             | 3.792            | 9.504 | 2.507  |
| S\textsubscript{0.05}Zn\textsubscript{0.01}/TiO\textsubscript{2} | 100           | 11.1             | 3.793            | 9.471 | 2.497  |

3.2. Photocatalytic degradation of toluene
Photocatalytic degradation of gaseous toluene was investigated in a continuous-flow reactor. Figure 1 shows the removal efficiencies of toluene by various photocatalysts (operating conditions: [O\textsubscript{2}] = 21%,...
[toluene] = 2 ppm, [RH] = 60%, residence time = 30 sec, Temp. = 35°C). The degradation results show that co-doped TiO$_2$ have better photocatalytic activities compared to S-doped TiO$_2$ and bare TiO$_2$. Among them, S$_{0.05}$Zn$_{0.0001}$/TiO$_2$ exhibits the highest photocatalytic activity. The higher degradation rates of toluene by S$_{0.05}$Zn$_{0.0001}$ and S-doped TiO$_2$ may be caused by the substitution of Ti atoms by sulfur atoms to form Ti–O–S bonds in TiO$_2$. The formation of Ti–O–S possibly leads to band gap narrowing, and then increases the absorption of visible light irritation. However, lower photocatalytic activities of photocatalysts with zinc contents above 0.0001% are obtained. The phenomena is ascribed to that active sites of photocatalyst surface are occupied by excess zinc. Therefore, S$_{0.05}$Zn$_{0.0001}$/TiO$_2$ was chosen to further study its photocatalytic reaction.

3.3. Gaseous products and byproducts by FTIR
In order to investigate byproducts and products of toluene photodegradation, a series of FTIR observations have been performed and the results are shown in Figures 2. IR spectra were demonstrated with reference from the database (Linstrom and Mallard, 2001). The relative humidity were set at two levels (RH = 0, 60% with [toluene]$_{in}$ = 2 ppm). The absorption peaks around 3,500–4,000 and 1,350–1,900 cm$^{-1}$ are attributed to H$_2$O, which is formed during the photocatalytic degradation of toluene or water vapor originally in the gas stream. The peaks intensity of water presents higher strength in a wet condition than in a dry condition. The absorption spectra located at 3,067 and 3,100 cm$^{-1}$ are the characteristic peaks of butadiene. The absorption bands assigned at about 2,955, 3,011, and 1,270 cm$^{-1}$ are attributed to acetone. The band at about 2,360 is assigned to gaseous CO$_2$. The toluene is observed at about 1,100 cm$^{-1}$. The broad absorbance in the range between 740 and 870 cm$^{-1}$ can be assigned to benzyl alcohol. The absorption bands at about 640–660 cm$^{-1}$ are characterizing of acetic acid.

![Figure 1](image_url)
3.4. Reaction pathway

The decomposition of toluene occurs by attacking from superoxide or hydroxyl radicals, and its selectivity strongly depends on the reaction conditions. Superoxide anion radicals and electrons (•O₂⁻/e⁻) play the key roles for the rate limiting step of the reaction in low level humidity. In a high level humidity, hydroxyl radicals and holes (•OH/h⁺) are the key roles. Figure 3 illustrates two potential reaction pathways in dry and wet condition. In the case of dry condition, the production of photo-induced electrons and holes is achieved when a lamp is turned on. The negatively charged electrons react with adsorbed oxygen molecules to form superoxide radicals. At the beginning of the experiment, benzyl radical (•C₇H₇) may be formed through •O₂⁻ radical attack [6]. The •O₂⁻ radical attack also leads to the formation of a long chain volatile organic compound. A further attack by •O₂⁻/e⁻, those byproducts can generate benzylperoxy radical, benzyl alcohol, benzaldehyde, benzoic acid, and long-chain organic compounds. The •O₂⁻/e⁻ attack also results in the formation of Acetone or butadiene. Acetone and butadiene are also oxidized by •O₂⁻ to form acetic acid, carbon dioxide, and water. Hydroxyl radicals are considered the key species for the wet reaction process. The positively charged holes generate hydroxy radicals (•OH) by reacting with adsorbed water, and then initiate the oxidation of the adsorbed organic compounds. The reaction pathway of the wet condition is similar to that for a dry condition except that it may generate cresols no production of benzylperoxy radical and aromatic bridged peroxy intermediate.
Figure 3. Proposed reaction pathways for photocatalytic conversion of toluene in dry and wet condition

4. Conclusion
The results show that S,Zn co-doped TiO$_2$ can reduce the crystalline size of the photocatalysts. S$_{0.05}$Zn$_{0.0001}$/TiO$_2$ exhibits the best decomposition rate for toluene. The decomposition rate of toluene decreases with increasing relative humidity and decreasing temperature. The products of the toluene photocatalytic oxidation are CO$_2$ and water; the by-products include benzaldehyde, benzyl alcohol, benzoic acid, acetone, butadiene and acetic acid. Superoxide radicals and •OH radical are considered the key species for the dry and wet reaction process, respectively.

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