Effect of Ga in the photocatalytic properties of TiO$_2$

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Abstract In this work we prepared a series of GaZn/TiO$_2$ (5 wt%, 10 wt%, and 15 wt% of Ga) photocatalysts by the sol-gel method. The X-ray diffraction results showed the presence of TiO$_2$ in anatase phase. Also, in the GaZn/TiO$_2$ system a small peak assigned to Ga$_2$O$_3$ is present. The specific surface area of the Zn/TiO$_2$ is 97 m$^2$/g and the specific surface area increases to 132 m$^2$/g when the amount of Ga increases. The energy band gap values obtained by UV-VIS diffuse reflectance spectroscopy are 2.9, 3.12 and 3.15 eV for 5GaZn/TiO$_2$, 10GaZn/TiO$_2$ and 15GaZn/TiO$_2$ respectively. The results of the photocatalytic activity show that the total destruction of phenol is more efficient in GaZn/TiO$_2$ than in the Zn/TiO$_2$ photocatalysts.

1. Introduction.

Semiconductors, such as TiO$_2$, ZnO, ZnS, and SnO$_2$, have been applied as photocatalysts [1]. Among them, TiO$_2$ is reported as the most promising one because of its high efficiency, stability, and low cost. In recent years, attention has been diverted to metal-doped TiO$_2$, which is believed to decrease the band-gap energy. The beneficial effects of the Zn-doping of TiO$_2$ catalysts have already been reported in wastewater treatment [2,3] and dye sensitized solar cells [4]. We have selected the Zn–TiO$_2$ because: (a) it has a large contact area to deposit gallium on Zn–TiO$_2$, (b) it is resistant to the heat treatment required during the solid state synthesis and (c) it is not attacked by highly oxidative radicals produced during the photocatalytic process.

The Ga$_2$O$_3$ is a semiconductor with a wide band gap (4.8 eV) and its electronic and luminescent properties have been reported [5,6]. The Ga$_2$O$_3$-TiO$_2$ composite oxide was also reported to be an interesting material having numerous applications in the areas of photocatalysis, electrocatalysis, and materials science [7,8]. In this work, ZnTiO$_2$ (anatase) samples are modified with a Ga$^{3+}$ in 5% 10, and 15% Ga respectively by sol-gel method and tested for a probe reaction, i.e. phenol photo-oxidation out
in the aqueous system. From the residual photocatalysts have been determined their crystalline phases by X-ray diffraction (XRD), specific surface areas by BET and semiconductor properties by diffuse reflectance spectra.

2. Experimental

2.1. Synthesis

The GaZn/TiO$_2$ catalysts were prepared by sol-gel method using titanium butoxide (Aldrich 99.99%), ethanol (99.9% Proquim) and HNO$_3$ (0.1M) was added under continuous stirring to give pH 3. The reaction mixture was heat at 70 °C and appropriate amounts of a solution of Zn(NO$_3$)$_2$ (Aldrich 99.99%), to obtain the Zn/TiO$_2$ with 5%wt. Appropriate amounts of Ga(NO$_3$)$_3$ were added to obtain GaZn/TiO$_2$ powders at 5, 10 and 15% wt of Ga (5GaZn/TiO$_2$, 10GaZn/TiO$_2$ and 15GaZn/TiO$_2$ samples) Then, samples were dried in vacuum for 24 h at 70 °C. Finally they were annealed at 400°C during 4 h in air. A TiO$_2$ reference sample was prepared in the same way.

2.2. Characterization

Once the powders were obtained, they were characterized by means of the UV-Vis absorption spectra with a Cary-III spectrometer equipped with a diode array as detector. FTIR characterization was made using a Brucker spectrometer (Vertex 70). X-ray diffraction patterns were recorded by a diffractometer Bruker Advance D-8. Textural properties were determined from the nitrogen adsorption isotherms obtained with a Quantachrome Autosorb-3b.

2.3. Photocatalytic Activity

The photocatalytic activity studies of the samples were carried out as follows: 500 mg of catalyst was added to an aqueous solution of phenol (280 ppm, 200 mL) in air flux (0.5 L min$^{-1}$), the reactor used in all experiments was a 500 mL Pyrex glass vessel and the temperature of the system was 30 °C (± 1°C). All experiments were carried out under similar conditions of solar irradiation, i.e., on relatively cloudless days to minimize differences in the degradation due to widely different experimental conditions of photon flux. The experiments were typically initiated at 11:00 a.m. at 2:00 p.m. with a total period of solar exposure (reaction) of 8 hours. The reaction rate was followed by taking samples every 45 min; and analyzing them in a Cary-III spectrometer. The concentration of phenol was calculated from the absorption band at 270 nm by means of a phenol calibration curve.

3. Results and discussion

Fig. 1 shows the nitrogen adsorption-desorption isotherms for the 5GaZnTiO$_2$, 10GaZnTiO$_2$, and 15GaZnTiO$_2$ samples. This figure shows that the isotherms are type IV for the catalysts according to the BDDT (Brunauer, Deming, Deming) classification. Their hysteresis loops are of type H2 and H1 respectively according to the IUPAC classification [9]. The Brunauer- Emmett-Teller (BET) surface area calculations gave a surface area the 133 m$^2$/g for 15GaZnTiO$_2$, 132 m$^2$/g, and 113 m$^2$/g for 10GaZnTiO$_2$ and 5GaZnTiO$_2$ respectively (Table 1) and they are higher than the Zn/TiO$_2$ sample. The doped Ga exists mostly in the form of Ga$_2$O$_3$ on the surface of ZnTiO$_2$ by surface doping, although substitutional doping may also be possible.

X-ray diffraction (XRD) patterns of the ZnTiO$_2$ doped with gallium ions are shown in Fig. 2. These spectra show peaks at the 2θ values: 25.4°, 37.8°, 48.2°, 54.0°, and 55.2° which correspond to anatase (101), (004), (200), (105), and (211) crystal planes, respectively. In the XRD pattern of GaZnTiO$_2$ a small peak at 30.65° is assigned to Ga$_2$O$_3$ [10] due to the incorporation of Ga ions in the Zn/TiO$_2$ lattice during the synthesis process. This peak increases as the concentration of Ga ions is increased. The Figure 3 shows the FTIR spectra of several samples. All the samples show a strong absorption band at 1100 cm$^{-1}$, which is assigned to internal vibration of TiO$_4$ tetrahedra and the peak at 550 cm$^{-1}$ assigned to double five-ring vibration. However, we did not find the absorption bands of stretching vibrations of bridged hydroxyls related to tetrahedrally coordinated framework gallium at ca. 3615 cm$^{-1}$.
to 3625 cm\(^{-1}\) for any of the gallosilicate structures [11], which suggests that the gallium species did not incorporate into the framework tetrahedral sites of ZnTiO\(_2\).

Table 1. Specific surface area (SA), pore volume (\(V_p\)) and average pore size (\(\Phi_p\)) of GaZn/TiO\(_2\) system.

| Samples      | SA (m\(^2\)/g) | \(V_p\) (cc/g) | \(\Phi_p\) (Å) |
|--------------|---------------|---------------|---------------|
| 5GaZnTiO\(_2\) | 113           | 0.208         | 73.53         |
| 10GaZnTiO\(_2\) | 132          | 0.227         | 68.28         |
| 15GaZnTiO\(_2\) | 133          | 0.175         | 52.80         |
| 5Zn/TiO\(_2\) | 105.2         | 0.217         | 75.22         |

Figure 1. Nitrogen adsorption isotherms for the (■) 5GaZn/TiO\(_2\), (▲) 10GaZn/TiO\(_2\) and (◊) 15GaZn/TiO\(_2\) samples.

Figure 2. X-ray patterns for the (a) 5GaZn/TiO\(_2\), (b) 10GaZn/TiO\(_2\) and (c) 15GaZn/TiO\(_2\) samples.

Figure 3. FTIR spectra for the (a) 5GaZn/TiO\(_2\), (b) 10GaZn/TiO\(_2\) and (c) 15GaZn/TiO\(_2\) samples.

Figure 4 UV-Vis spectra for the (a) Zn/TiO\(_2\), (b) 5GaZn/TiO\(_2\), (c) 10GaZn/TiO\(_2\) and (d) 15GaZn/TiO\(_2\) samples.
An additional shoulder emerges at ca. 3795 cm\(^{-1}\) for Ga-modified ZnTiO\(_2\), it is assigned to the vibration of hydroxyls located at non framework gallium species [12] and it increases in intensity when of gallium content increases.

When the loading amount is low, the hydrated Ga\(^{3+}\) cations are closely restricted to the outer surface of the ZnTiO\(_2\) crystals, and they rarely have the chance to gain access to the position inside the ZnTiO\(_2\) pores [13]. As the loading amount increases, most exchangeable outside sites are occupied and the Ga\(^{3+}\) cations have more chance to access to the pores and locate near the mouth of pore. It may be the reason that the activity increased with the increase of loading amount only at the gallium.

Table 2. Band gap values and Results of the Langmuir–Hinshelwood model for phenol decomposition on sol–gel catalysts of GaZn/TiO\(_2\)

| Samples          | Eg (eV) | \(k_1 \times 10^6\) (min\(^{-1}\)) | \(k_2\) (M\(^{-1}\)) | \(k_1k_2\) (min\(^{-1}\) M\(^{-1}\)) |
|------------------|---------|-----------------------------------|-----------------------|----------------------------------|
| 5Zn/TiO\(_2\)    | 2.9     | 5.59                              | 2450                  | 0.014                            |
| 5GaZnTiO\(_2\)   | 3.12    | 6.93                              | 3039                  | 0.021                            |
| 10GaZnTiO\(_2\)  | 3.15    | 9.4                               | 4040                  | 0.039                            |
| 15GaZnTiO\(_2\)  | 3.30    | 11.92                             | 5162                  | 0.062                            |

The absorption spectra of the 15GaZn/TiO\(_2\), 10GaZn/TiO\(_2\) and 5GaZn/TiO\(_2\) and Zn/TiO\(_2\) samples (Fig. 4) shows an increment in the absorption in the interval from 700 to 400 nm which is due to the absorption of the Ga\(_2\)O\(_3\) [14]; the interval from 400 to 350 nm and is due to the TiO\(_2\) fundamental absorption.

The band gap energy (Eg) of the samples were calculated by the equation \(\alpha(h\nu)=A( h\nu- Eg)^m/2\), where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy, A is a constant and \(m = 1\) represents a direct transition between bands [15]. The band gap energies were 2.9, 3.12 and 3.15 eV for 15GaZn/TiO\(_2\), 10GaZn/TiO\(_2\) and 5GaZn/TiO\(_2\) respectively (Table 2).

The importance of the measured of the band energy resides in that; the rate that electron-hole are generated is determined first by irradiation conditions such as photon energies and fluxes, and secondly by optical absorption characteristics of the photocatalytic particles such as their band gap.

The photocatalytic activity of the samples was studied using, as a test reaction, the decomposition of the phenol. The results obtained by UV-Vis spectra of the phenol as a function of time of sun exposure (reaction) with 15GaZnTiO\(_2\) photocatalysts is shown in Fig. 5. These spectra show a significant decrease in phenol absorbance (85% in 270 min). Also, no apparent new absorbance peaks, indicating near complete mineralization of phenol. The behavior of the other catalysts is similar to the 15GaZnTiO\(_2\) sample, but percentage of phenol decomposition is lower to the 15GaZnTiO\(_2\) catalyst at the same time (270 min) and the concentration of phenol diminishes slowly when the reaction takes place without catalyst (Fig. 6).

For the correct evaluation of data we applied the Langmuir–Hinshelwood model using the integrated equation for heterogeneous photocatalytic reactions in a batch reactor [15,16].

\[
\ln \frac{C_0}{C} = -k_2 + \frac{mAk_1k_2t}{V(C-C)}
\]

where, \(V\) is the liquid volume, \(C\) the substrate concentration, \(t\) the time, \(m\) the mass of catalyst, \(A\) the adsorption sites per g of catalyst, \(k_1\) the apparent rate constant and \(k_2\) the apparent adsorption constant. The values of \(k_1, k_2, k_1k_2\) (apparent reactivity) for the catalysts obtained at different temperatures in the decomposition of phenol are tabulated in Table 2. These data were estimated from a graph of \((\ln(C/C_0))/C_0\) against \(t/(C_0-C)\). The activity for the catalyst 15GaZnTiO\(_2\) shows that degradation is favored and according to the high \(k_2\) value we can see that the adsorption capacity of this catalyst is favored due to its higher degree of hydroxylation, hence the OH groups behave as adsorption centers.
observed from FTIR spectra (see Figure 3). When the Ga$^{+3}$ ion doping is increased in the ZnTiO$_2$ the photocatalytic activities is increased, since the oxide metal incorporation influences the photo reactivity of catalyst by acting as holes traps and by altering the e$^-$/h$^+$ pair recombination [17-18].

![Figure 5](image_url)  
**Figure 5.** UV-Vis spectra of the phenol as a function of time of sun exposure (reaction) with 15GaZn/TiO$_2$ catalyst.

![Figure 6](image_url)  
**Figure 6.** Photocatalytic degradation of phenol a) without catalysts b) ZnTiO$_2$, c) 5GaZnTiO$_2$ d) 10GaZnTiO$_2$ and e) 15GaZnTiO$_2$.

4. Conclusion
Photocatalytic processes by a GaZn/TiO$_2$ catalyst are quantitatively efficient in the decomposition of the water-soluble phenol fraction. The total destruction of water-soluble compounds originating from phenol indicates that the photocatalysis can be employed for water treatment. The process proposed in this investigation uses non-expensive materials for the construction of the catalysts.

5. References.
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