Title: Sol-gel preparation and characterisation of SnO₂ powders employed as catalyst for phenol photodegradation

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Abstract
Crystallized pure SnO₂ powders were prepared by the sol-gel process and were used as photocatalyst for the degradation of phenol under UV light at pH 6.5 and a temperature of 20°C. The physical properties of photocatalyst were characterized by X-ray diffraction, Scanning Electron Microscopy, nitrogen adsorption-desorption and Ultraviolet-visible diffuse reflectance spectroscopy. The influences of different operating variables such as the pH, the photocatalyst loading, the initial concentration of phenol, were studied to improve the efficiency of phenol degradation.

Keywords: Tin dioxide; Sol–gel; Photocatalysis; Phenol degradation.

1. Introduction

Heterogeneous photocatalysis is nowadays recognized as a strategic area of growing importance in what concerns the development of sustainable technologies for energy production and storage [1], green chemical synthesis [2], and water [3] and air [4] treatments. Indeed, upon band gap excitation of the photocatalyst (semi-conductor), the photoinduced electrons and positively charged holes can reduce and oxidize the species adsorbed on the semiconductor particles [5-7].

Phenol and its derivatives are toxic hazardous compounds because they are suspected to be carcinogens and are known as precursors of dioxins. They often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Because of their toxicity and poor biodegradability, phenolic wastewaters must be specially treated before disposing off.
Various treatment techniques have been applied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation [8], solvent extraction [9], membrane techniques [10], adsorption [11], coagulation-flocculation [12], biological processes [13], and photodegradation [14]. So, heterogeneous photocatalysis with semiconductor particles represents an attractive solution for the degradation of phenol at room temperature [15, 16].

SnO$_2$, semi-conductor with a band gap equal to 3.6 eV [17], is used in several applications such as gas sensors, photocaptors, antistatic films, oxidation catalysts because of its interesting optical properties, its transparency in visible range and its very high chemical stability [18]. Furthermore, the dual valency of SnO$_2$ facilitates a reversible transformation of the surface composition from stoichiometric surfaces with Sn$^{4+}$ surface cations into a reduced surface with Sn$^{2+}$ surface cations depending on the oxygen chemical potential of the system and on the size of SnO$_2$ particles [19]. These redox phenomena present at the surface of SnO$_2$ are particularly attractive for photocatalytic applications such as the phenol photodegradation.

It is particularly interesting to synthesize SnO$_2$ by the sol-gel process because sol-gel chemistry is an efficient tool for controlling morphology and reactivity of solids. In recent decades, it has permitted the development of new highly dispersed materials, presenting both good homogeneity and purity [20-22].

The first aim of this work is to synthesize a crystallized pure SnO$_2$ powder by the sol-gel process. SnO$_2$ powder is characterized by using techniques such as nitrogen adsorption isotherms, X-Ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis spectroscopy. The second aim of this work is to study the degradation of phenol on SnO$_2$ photocatalyst and to establish the relationships between operating variables such as the pH, the photocatalyst loading, the initial concentration of phenol, and the efficiency of phenol degradation.

2. Experimental section

2.1. Photocatalyst preparation

37 mmol of SnCl$_2$ (Aldrich, Purity: 99.99%) was mixed in 100 mL of absolute ethanol (Merck, Purity: 99.9%) under stirring and refluxed at 80°C under nitrogen ambient in a closed vessel for 2 h. A white tin alkoxide powder was obtained after heating of solution at 80°C under vacuum condition [23], to which 50 mL of absolute ethanol and 50 mL of distilled water were added. This solution was then stirred and heated for 2 h at 50°C. The stirring was stopped and gelation underwent in about 5 days. Afterwards, the gel was dried at
110°C for 2h. Finally, the powder was calcined under flowing air (0.1mmols⁻¹) at 700°C for 4h.

2.2. Photocatalyst characterization

Nitrogen adsorption-desorption isotherms were measured at -196°C on a Fisons Sorptomatic 1990 after outgassing for 24 h at ambient temperature.

SnO₂ particles sizes were examined by SEM on a Jeol JSM-840 under high vacuum, at an acceleration voltage of 20 kV. The samples were deposited onto carbon tape and coated with gold in a Balzers plasma sputterer (30 s at 30 mA).

XRD was used to determine the nature and the size of crystalline phases of SnO₂. Patterns were obtained with hand-pressed samples mounted on a Philips PW 1830 goniometer using the Cu-Kα line (λ=0.15458 nm).

Diffuse reflectance measurements in the UV/Vis region (250–800 nm) were performed on a Varian Cary 5000 UV/Vis/NIR spectrophotometer, equipped with a Varian External DRA-2500 integrating sphere, using BaSO₄ as the reference. Spectra were recorded in diffuse reflectance mode (R = reflection intensity) and were transformed into the absorbance coefficient (F(R)) by the Kubelka–Munk function, F(R) = (1 - R)²/2R [24]. SnO₂ band gap energy value, Eg, was obtained by extrapolating the straight line portion of the plot to zero absorption coefficient.

The PZC (Point of zero charge) of SnO₂, that is the pH value at which the electrical charge density on the support surface is zero, was determined by the method of Park and Regalbuto (equilibrium pH at high loading, EpHL) [25]: the solid material is soaked in water solutions of various starting pHs and after stabilization, the pH is measured again. The PZC of the solid corresponds to a plateau in a plot of the final pH vs. the initial pH. Using a spear-tip semi-solid electrode (Electrode Accumet), the equilibrium pH of SnO₂ was measured over a wide range of initial pH values (from pH = 1 to pH = 13) adjusted using either HCl or NaOH solutions.

2.3. Photocatalytic experiments

To determine the photocatalytic activity of the synthesized material, the study of the degradation of phenol (Riedel-de Haën, Purity: 99.5%) under UV irradiation was realized.

The phenol degradation was carried out at 20°C using a water-cooled cylindrical 200 mL glass reactor with external lamp (125 W UV lamps, Black light Mercury HgV). In a first time, the amount of catalyst powder, [SnO₂], was kept at 0.1 g L⁻¹, the initial concentration of phenol, C₀, was 0.2 g L⁻¹ and the pH of the solution was fixed to 6.5. In a second time, photocatalytic experiments were realized with varying operating variables: three different pH
values (2.5, 6.5 and 12.5) adjusted with aqueous solutions of HCl and NaOH (2 mol L$^{-1}$), ten photocatalyst concentrations [SnO$_2$] (from 0.2 to 2.0 g L$^{-1}$) and five initial concentrations of phenol, C$_{0}$ (from 0.05 to 0.25 g L$^{-1}$).

Before each photocatalytic test, the mixture was kept in the dark for 1h to ensure that the adsorption–desorption equilibrium was reached before illumination. The sample was then taken out at the end of the dark adsorption period, just before the light was turned on, in order to determine the phenol concentration in solution, C$_{0}'$. In all cases, the difference between C$_{0}$ and C$_{0}'$ were found to be negligible when compared to the error of the method.

When the lamp was turned on, the experiment started. After a given irradiation time, the sample was taken out from reactor, then the catalyst [SnO$_2$] was removed by centrifugation and the remaining phenol concentration in the solution was measured with the photocoulometric method of 4-amino-antipirine [26], analyzed with a 1201 Shimadzu spectrophotometer.

Repetition tests were made to ensure the reproducibility of results. So the all photocatalytic results presented in this work are the mean of three replicates.

3. Results and discussion

3.1. Synthesis of crystallized pure SnO$_2$ by the sol-gel process

The crystallization of the calcined SnO$_2$ powder was checked by X-ray diffraction. In Fig. 1, all the peaks [JCPDS Powder Diffraction File Card 5-0467] corresponding to tetragonal SnO$_2$ (a = b = 0.4731 nm and c = 0.3173 nm) are observed. The mean size of SnO$_2$ crystallites is calculated from Scherrer’s formula based on line broadening analysis [27] and is equal to around 36 nm.

By SEM analysis, it is observed in Fig. 2a that the calcined SnO$_2$ powder is composed of aggregates of SnO$_2$ particles. The mean size of SnO$_2$ particles is equal to 50 nm (Fig. 2b) and is in agreement with the SnO$_2$ particle size calculated from XRD measurements.

A nitrogen adsorption-desorption isotherm was carried out to analyze the textural properties of the calcined SnO$_2$ powder and it is presented in Fig. 3. This isotherm displays a slight increase of the adsorbed volume at very small p/p$_0$ values, which is characteristic of the presence of micropores (< 2 nm) inside SnO$_2$ particles [28]. Furthermore, the isotherm shows a hysteresis at p/p$_0$ from 0.4 to 1, due to capillary condensation in mesopores (2-50 nm) corresponding in the voids between the 30-50 nm SnO$_2$ powder particles [28]. Finally, the specific surface area obtained by the BET method [28] of the calcined SnO$_2$ powder is equal to 25 m$^2$ g$^{-1}$, characteristic of a material with low porosity or a crystallized material [6, 7].
Calculated from UV/Vis measurements, the Kubelka–Munk function \((F(R)E)^{1/2}\) as a function of energy level \(E\) for the calcined \(\text{SnO}_2\) powder, is shown in Fig. 4. The sample displays a band-gap value, \(E_g = 3.6\) eV, which is the band gap of a crystallized pure \(\text{SnO}_2\) semi-conductor [17]. This sample is also characteristic of a photoactive material in UV region \((\lambda < 380\) nm) [7].

Because one of the aims of this work is to determine the relationships existing between the initial pH of phenolic solution and the degradation of phenol, it is very important to know the PZC of the calcined \(\text{SnO}_2\) powder. The PZC of the calcined \(\text{SnO}_2\) powder is shown in Fig. 5. This curve clearly shows a plateau at 6.52. The hydroxyl (-OH) groups that populate \(\text{SnO}_2\) surface become protonated and so positively charged below 6.52, while the same hydroxyl groups become deprotonated and negatively charged above this characteristic pH value. So a \(\text{SnO}_2\) powder placed in solutions at pH values below 6.52 adsorbs anions, while at pH values above 6.52, the same support adsorbs cations.

### 3.2. Photocatalytic activity of the calcined \(\text{SnO}_2\) powder

#### 3.2.1 Kinetic study

In Fig. 6 is shown the photodegradation of phenol in contact with the calcined \(\text{SnO}_2\) powder as a function of time with following operating variables: three different pH values for the phenolic solution (2.5; 6.5 and 12.5), \([\text{SnO}_2] = 0.2\) g L\(^{-1}\) and \(C_0 = 0.1\) g L\(^{-1}\). For \(pH = 6.5\), which is the PZC of the calcined \(\text{SnO}_2\) powder, for the first 40 min, the phenol photodegradation is fast: about 40% of phenol was degraded. Afterwards, the phenol photodegradation rate decreases: about 10% of phenol was degraded for the following 80 min.

This decrease of the phenol degradation rate could be the consequence of the formation of by-products of phenol such as hydroquinone and catechol, strongly adsorbed at the surface of the photocatalyst, as explained in [29]. So these by-products compete with phenol for adsorption sites on the surface of \(\text{SnO}_2\) and the phenol degradation is slowed down.

#### 3.2.2 pH effect

At the time of phenol photodegradation, the decomposition targets are organic compounds that usually are anionic electron donors or neutral. At low pH (pH < 6.52), the positively charged tin hydroxide provides suitable surface for chemisorption of organic compounds. The organic compounds are adsorbed on the surface and are attacked directly by positive holes of valence band: the direct charge transfer is predominant with an increase of the degradation photoactivity [29]. Indeed, in Fig. 6, at \(pH = 2.5\), it is observed a slightly increase of the rate of phenol degradation: after 120 min, about 60% of phenol is eliminated from the wasted water. At high pH (pH > 6.52), on the contrary, the organic compounds
mainly are attacked by free activated oxidant species. The free activated oxidant species are supposed to exist in the aqueous phase adjacent to the surface of SnO$_2$ because they cannot disperse far into the water due to short lifetime [29]: mass transfer limitations of phenol appear early at the surface of the photocatalyst and the photocatalytic activity decreases. Furthermore, in a basic medium, phenol becomes the anion phenolate (C$_6$H$_5$O$^-$), for which it is nearly impossible to be adsorbed on the negatively charged surface of SnO$_2$. Therefore, the photocatalytic efficiency decreases. This trend is observed in Fig. 6 because at pH = 12.5, only about 25% of phenol is degraded after 120 min. From these results, the pH of the initial phenolic solution was adjusted to 2.5 for the following degradation measurements presented below.

3.2.3 Effect of catalyst concentration

In order to avoid an ineffective excess of catalyst and to ensure a total absorption of efficient photons, the optimum mass of the SnO$_2$ photocatalyst needs to be found. In this work, [SnO$_2$] was varied from 0.2 to 2.0 g L$^{-1}$ at pH = 2.5 and C$_0$ = 0.1 g L$^{-1}$.

As shown in Fig. 7, the residual phenol fraction after 120 min in the solution, (C/C$_0$)$_{120}$, decreases with an increase of the mass of catalyst up to an amount of 1.0 g L$^{-1}$. This behaviour can be associated to an increment of the active sites available for phenol degradation [30]. However, an increase on the catalyst loading to 2.0 g L$^{-1}$ results in a slight increase of (C/C$_0$)$_{120}$, which can be attributed to a screening effect due to the redundant dispersion of UV radiation caused by the substantial amount of suspended photocatalyst. Furthermore, in these conditions, particles of SnO$_2$ tend to agglomerate, making a significant fraction of the catalyst to be inaccessible to absorbing the radiation, with consequent decrease in the active sites available to the catalytic reaction [30].

3.2.4 Effect of phenol concentration

The initial phenol concentration, C$_0$, was varied from 0.05 to 0.25 g L$^{-1}$ at pH = 2.5 and with [SnO$_2$] = 1.0 g L$^{-1}$. Results are presented in Fig. 8. It is observed that (C/C$_0$)$_{120}$ slightly decreases when C$_0$ increases from 0.05 to 0.20 g L$^{-1}$. This behaviour can be associated to an increment of adsorbed phenol on the photocatalyst surface, which is followed by the degradation of phenol. We note (C/C$_0$)$_{120}$ begins to increase when C$_0$ is increased to 0.25g.L$^{-1}$. This observation is in agreement with previous studies [29, 30]: as phenol concentration increases, more reaction intermediates (catechol, hydroquinone) are adsorbed on the surface of the photocatalyst. Therefore, these by-products compete with phenol for adsorption sites on the surface of SnO$_2$ and the phenol degradation is slowed down.
4. Conclusions

The sol-gel process used in this work allowed producing a crystallized pure SnO$_2$ powder after a calcination step. This calcined SnO$_2$ powder was very active for the degradation of phenol under UV irradiation.

The photocatalytic process was influenced by several operating variables such as pH of the solution, catalyst loading and initial phenol concentration. In this work, it was established that the use of a pH = 2.5 for the medium, a SnO$_2$ concentration = 1.0g L$^{-1}$ and initial phenol concentration = 0.20g L$^{-1}$ allowed the degradation of about 60% of phenol after 120 min.

These first results being interesting, the degradation of phenol by-products, such as catechol and hydroquinone, is actually studied on SnO$_2$ photocatalyst synthesized by the sol-gel process.

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References


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**Figure(s)**

Figure 1: XRD pattern of the calcined SnO\(_2\) powder.

Figure 2: SEM micrograph of the calcined SnO\(_2\) powder, (a) 2000 X and (b) 10.000 X.

**Figure 3:** Nitrogen adsorption-desorption isotherm of the calcined SnO\(_2\) powder.

**Figure 4:** Determination of Eg of the calcined SnO\(_2\) powder.

**Figure 5:** PZC determination of the calcined SnO\(_2\) powder.
Figure 6: Degradation of phenol as a function of time, where $C_0$ is the initial phenol concentration (g L$^{-1}$) and $C$ is the phenol concentration at the time $t$. $C_0 = 0.1$ g L$^{-1}$, [SnO$_2$] = 0.2 g L$^{-1}$, pH = 2.5 (▲), pH = 6.5 (■) and pH = 12.5 (♦).

Figure 7: Residual fraction of phenol after 120 min, $(C/C_0)_{120}$, as a function of the SnO$_2$ powder concentration in the suspension. $C_0 = 0.1$ g L$^{-1}$ and pH = 2.5.

Figure 8: Residual fraction of phenol after 120 min, $(C/C_0)_{120}$, as a function of the initial phenol concentration, $C_0$. [SnO$_2$] = 1.0 g L$^{-1}$ and pH = 2.5.