

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

Hadj Benhebal^{1*}, Messaoud Chaib¹, Angélique Léonard², Ludivine Tasseroul², Carlos A. Paèz², Thierry Salmon², Dirk Poelman³, Michel Crine², Benoît Heinrichs², Jean-Paul Pirard², Stéphanie D. Lambert²

¹Laboratoire de Chimie et Environnement, Université de Tiaret, BP 78 Zaaroura, Tiaret 14000, Algeria.

²Laboratoire de Génie chimique, B6a, Université de Liège, B-4000 Liège, Belgium

³Ghent University, Lumilab, Department of Solid State Sciences, Krijgslaan 281-S1, B-9000 Ghent, Belgium.

*To whom correspondence should be addressed. Tel/Fax: +213 46 45 20 63

E-mail : benhebalh@yahoo.fr

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].

SnO₂, 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 SnO₂ facilitates a reversible transformation of the surface composition from stoichiometric surfaces with Sn⁴⁺ surface cations into a reduced surface with Sn²⁺ surface cations depending on the oxygen chemical potential of the system and on the size of SnO₂ particles [19]. These redox phenomena present at the surface of SnO₂ are particularly attractive for photocatalytic applications such as the phenol photodegradation.

It is particularly interesting to synthesize SnO₂ 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 SnO₂ powder by the sol-gel process. SnO₂ 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 SnO₂ 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 SnCl₂ (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 cristalline phases of SnO₂. Patterns were obtained with hand-pressed samples mounted on a Philips PW 1830 goniometer using the Cu-K_α line ($\lambda=0.15458$ 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, E_g , 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, E_{pHL}) [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, C_0 , 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 [SnO₂] (from 0.2 to 2.0 g L⁻¹) and five initial concentrations of phenol, C₀ (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, C₀'. In all cases, the difference between C₀ and C₀' 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 [SnO₂] 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 SnO₂ by the sol-gel process

The crystallization of the calcined SnO₂ powder was checked by X-ray diffraction. In Fig. 1, all the peaks [JCPDS Powder Diffraction File Card 5-0467] corresponding to tetragonal SnO₂ (a = b = 0.4731 nm and c = 0.3173 nm) are observed. The mean size of SnO₂ 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 SnO₂ powder is composed of aggregates of SnO₂ particles. The mean size of SnO₂ particles is equal to 50 nm (Fig. 2b) and is in agreement with the SnO₂ particle size calculated from XRD measurements.

A nitrogen adsorption-desorption isotherm was carried out to analyze the textural properties of the calcined SnO₂ powder and it is presented in Fig. 3. This isotherm displays a slight increase of the adsorbed volume at very small p/p₀ values, which is characteristic of the presence of micropores (< 2 nm) inside SnO₂ particles [28]. Furthermore, the isotherm shows a hysteresis at p/p₀ from 0.4 to 1, due to capillary condensation in mesopores (2-50 nm) corresponding in the voids between the 30-50 nm SnO₂ powder particles [28]. Finally, the specific surface area obtained by the BET method [28] of the calcined SnO₂ powder is equal to 25m² 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 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 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 SnO_2 powder. The PZC of the calcined SnO_2 powder is shown in Fig.5. This curve clearly shows a plateau at 6.52. The hydroxyl (-OH) groups that populate 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 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 SnO_2 powder

3.2.1 Kinetic study

In Fig. 6 is shown the photodegradation of phenol in contact with the calcined 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), $[\text{SnO}_2] = 0.2 \text{ g L}^{-1}$ and $\text{C}_0 = 0.1 \text{ g L}^{-1}$. For pH = 6.5, which is the PZC of the calcined 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 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 ($\text{pH} < 6.52$), 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 ($\text{pH} > 6.52$), 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 SnO₂ 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 (C₆H₅O⁻), for which it is nearly impossible to be adsorbed on the negatively charged surface of SnO₂. 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 SnO₂ photocatalyst needs to be found. In this work, [SnO₂] was varied from 0.2 to 2.0 g L⁻¹ at pH = 2.5 and C₀ = 0.1 g L⁻¹

As shown in Fig. 7, the residual phenol fraction after 120 min in the solution, (C/C₀)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/C₀)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 SnO₂ 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, C₀, was varied from 0.05 to 0.25 g L⁻¹ at pH = 2.5 and with [SnO₂] = 1.0 g L⁻¹. Results are presented in Fig. 8. It is observed that (C/C₀)₁₂₀ slightly decreases when C₀ 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/C₀)₁₂₀ begins to increase when C₀ is increased to 0.25 g 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 SnO₂ and the phenol degradation is slowed down.

4. Conclusions

The sol-gel process used in this work allowed producing a crystallized pure SnO₂ powder after a calcination step. This calcined SnO₂ 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 SnO₂ 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 SnO₂ photocatalyst synthesized by the sol-gel process.

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Dr. Hadj Benhebal: received the diploma of engineer in industrial chemistry in 1993 from the University of Mostaganem (Algeria), the 3rd cycle doctorate in materials to the environment in 2004 from the University of Tiaret (Algeria) and The Ph.D. thesis in Sciences in chemistry of materials from the University of Sidi-belabbes (Algeria) in 2012 . Since 2004, he worked at the University of Tiaret as a teacher researcher. His research focuses on the treatment of water by various synthetic and natural materials.

Dr. Ludivine Tasseroul : received the M.Sc. in Vegetal Biology in 2006 from the University of Liege (Belgium), the M.Sc in Environmental Management in 2007 and her Ph.D. thesis in Sciences in the same university in 2012. At this moment, she works as a postdoctoral researcher in the Department of Chemical Engineering of the University of Liege. Her research interests are ecology, environmental management, new technologies for water purification and disinfection.

Dr. Carlos Alberto Paéz: received the M.Sc. in Chemistry in 2003 from the Industrial University of Santander (Colombia) and his Ph.D. thesis in Sciences in the same university in 2007. At this moment, he works as a postdoctoral researcher in the Department of Chemical Engineering of the University of Liege. His research interests are organic chemistry, homogeneous catalysis and photocatalysis.

Msc Ing.Ind. Thierry Salmon: received the Msc in Industrial Chemistry in 1983 from the Institut Supérieur Industriel of Bruxelles (ISIB). He manages the entire organisation of the laboratory, the building of the pilot plants and he supervises the technical part of the work of

the MSc and the PhD students. He also gives an help for the realisation of the analysis and the interpretation of the results.

Prof. Dr. Ir. LAMBERT Stéphanie D. : received the M.Sc. in Chemical Engineering from the University of Liege (Belgium) in 1999 and Ph.D. in Applied Sciences in the same university in 2003. She worked as a researcher engineer at Nanocyl Society in 2004. In 2005, she joined the Department of Chemical Engineering of the University of Liege as a FRS-FNRS postdoctoral researcher. From 2009, she became permanent as an Associate Professor and a FRS-FNRS Research Associate. Her research interests are heterogenous catalysis and catalytic reactors, synthesis by sol-gel process of mono- or bimetallic catalysts supported on inorganic xerogels, physico-chemical characterisation of support and metal active sites (texture, morphology, metal dispersion and localisation, nanoparticles composition in the case of bimetallic catalysts, surface composition of alloys, ...), development and optimisation of catalytic processes (hydrodechlorination, hydrogenation, oxidation of chlorinated volatile compounds, catalytic epuration of biogas, photocatalysis degradation of wastes in gaseous, aqueous and solid mediums).

Prof. Dr. Angélique Léonard : received the M.Sc. in Chemical Engineering from the University of Liege (Belgium) in 1998 and Ph.D. in Applied Sciences in the same university in 2002. In 2009, she was nominated as Professor in the Department of Chemical Engineering of the University of Liege. Her fundamental research activities are focussed on Treatment of wastewater sludge: Mechanical dewatering, Thermal drying, Optimisation of operating conditions, Influence of liming, Gaseous emissions and odours, Influence of sludge origin, Production of adsorbent materials from dried sludges. She also investigates on Flue gas treatment: Aerosol capture in filtering media, Adsorption of Volatile Organic Compounds on activated carbon, Flue gas cleaning in gas-liquid contacting units.

Prof. Dr. Messaoud Chaib: Research Professor at the University of Tiaret for over 20 years. Head of Chemistry and Environment Laboratory in the same University received the diploma of engineer in chemistry from the University of Boumerdes (Algeria) and Ph.D. in organique

chemistry in the University of Montpellier (France) in 1990. His fundamental research activities are focussed on field of Chemistry and Environment.

Prof. Dr. Ir. Heinrichs Benoît : received the M.Sc. in Chemical Engineering from the University of Liege (Belgium) in 1993 and Ph.D. in Applied Sciences in the same university in 1999. Between 1999 and 2007, he worked as an Assistant in the Department of Chemical Engineering of the University of Liege. In the end of 2007, he was nominated as Professor in the same department. His research interests are nanomaterials engineering (design and production), characterization and evaluation of nanomaterial properties. Since the morphology of a catalyst at the nanometer scale is a determining factor on its performances, the research aims at developing methods for the controlled synthesis of nanostructures dispersed inside porous materials and at evaluating their possible scale-up.

Prof. Dr. Ir. Pirard Jean-Paul : received the M.Sc. in Chemical Engineering from the University of Liege (Belgium) in 1970 and Ph.D. in Applied Sciences in the same university in 1974. Between 1974 and 1980, he worked as an Assistant in the Department of Chemical Engineering of the University of Liege. In 1981, he was nominated as Professor in the same department. His research interests are coal gasification, carbon nanotube synthesis, study of mass and heat transfer inside catalysts (local diffusion calculations, experimental tests to detect diffusional limitations, ...), study of the kinetics of catalytic reactions and of their mechanisms by fitting of phenomenological kinetic models on experimental data (experimental design, data statistical treatment, optimisation and statistical tests of models, ...).

Prof. Dr. Dirk Poelman studied physics and obtained his PhD in solid state physics at Ghent University (Belgium). Since 2001, he has a permanent appointment at Ghent University, where he is leading the research group Lumilab. He is a full professor since 2012. Dirk Poelman has experience in different fields of solid state physics research, including thin film deposition and optical characterization, photo-, electro- and cathodoluminescent materials,

structural and electrical defects in semiconductors, photocatalysis for air purification, x-ray analytical techniques and human vision. He has published about 125 papers in peer reviewed international journals.

Prof. Dr. Michel Crine : received the M.Sc. in Chemical Engineering from the University of Liege (Belgium) in 1972 and Ph.D. in Applied Sciences in the same university in 1978. Between 1981 and 1994, he became permanent in the Department of Chemical Engineering of the University of Liege as a FRS-FNRS Research Associate (1981-1989), a FRS-FNRS Senior Research Associate (1989-1993) and a FRS-FNRS Research Director (1993-1994) respectively. In 1994, he was nominated as Professor in the same department. His fundamental research activities have been for a long time focussed on the study of multiphase unit operations (catalytic trickle-bed reactors, biological trickling filters,...). A special attention has been paid to the experimental investigation of fluid flow hydrodynamics. Advanced experimental techniques have been developed to visualize non intrusively the local flow hydrodynamics, e.g., X-ray tomographic techniques and particle image velocimetry. Since 1994, research activities have been re-oriented towards gas-liquid absorption packed columns, distillation packed columns, as well as dewatering and drying techniques. More recently, research interests have been extended to the hydrodynamics in multiphase rheologically complex fluids (non newtonian fluids, pasty materials), such as those used in biotechnology, processing of agro-foods and drying of sludges.

Figure(s)

Figure 1: XRD pattern of the calcined SnO₂ powder.

Figure 2: SEM micrograph of the calcined SnO₂ powder, (a) 2000 X and (b) 10.000 X.

Figure 3: Nitrogen adsorption-desorption isotherm of the calcined SnO₂ powder.

Figure 4: Determination of E_g of the calcined SnO₂ powder.

Figure 5: PZC determination of the calcined SnO₂ 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 . $C_0 = 0.1 \text{ g L}^{-1}$, $[\text{SnO}_2] = 0.2 \text{ g L}^{-1}$. pH = 2.5 (\blacktriangle), pH = 6.5 (\blacksquare) and pH = 12.5 (\blacklozenge).

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. $C_0 = 0.1 \text{ g L}^{-1}$ 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 . $[\text{SnO}_2] = 1.0 \text{ g L}^{-1}$ and pH = 2.5.