Chemical Engineering Journal 264 (2015) 417–424

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Mesoporous TiO_2 nanocrystals as efficient photocatalysts: Impact of calcination temperature and phase transformation on photocatalytic performance

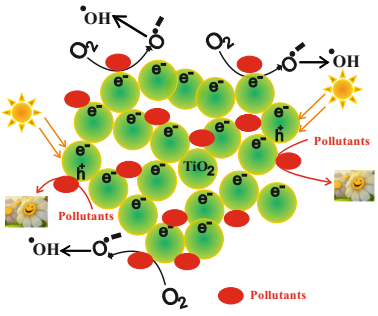
M. Faycal Atitar [a], Adel A. Ismail [b,c,*], S.A. Al-Sayari [c,e], Detlef Bahnemann [a], D. Afanasev [d], A.V. Emeline [d]

[a] Institut für Technische Chemie, Leibniz Universität Hannover, Callinstrasse 3, D-30167 Hannover, Germany
[b] Advanced Materials Department, Central Metallurgical R & D Institute (CMRDI), P.O. Box: 87 Helwan, Cairo 11421, Egypt
[c] Advanced Materials and Nano-Research Centre, Najran University, P.O. Box: 1988, Najran 11001, Saudi Arabia
[d] Department of Physics, University of St. Petersburg, UlianoVskaia 1, St. Petersburg 198904, Russia
[e] Department of Chemistry, College of Science and Arts-Sharoura, Najran University, Saudi Arabia

HIGHLIGHTS

- One-step synthesis of mesoporous TiO_2 was achieved at different temperatures.
- XRD can be indexed to the anatase and rutile phases for all prepared samples.
- Mesoporous TiO_2 exhibits ~2–3 times higher photoactivity than nonporous TiO_2.
- The behavior of the photocatalysts varies based on the pollutant type.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form 5 November 2014
Accepted 13 November 2014
Available online 22 November 2014

Keywords:
Mesoporous TiO_2
Calcination temperatures
Photodegradation
Herbicide imazapyr
Phenol

ABSTRACT

Mesoporous TiO_2 nanocrystals have been synthesized through sol gel method in presence of triblock copolymer as the structure directing agent. The as-prepared TiO_2 nanocrystals have been calcined at different temperatures, i.e., at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C to demonstrate how their structural properties (morphology, mesoporosity, crystallite phases and sizes) affect the photocatalytic performance. The TEM images indicate that TiO_2 nanocrystals calcined at 500 °C have a mesoporous structure with particle sizes of approximately 10–15 nm. However, the TiO_2 calcined at 800 °C shows a lower mesoporosity and particle sizes of ~75 nm. The photocatalytic performance of the newly synthesized photocatalysts has been evaluated through the photodegradation of two different pollutants, i.e., the herbicide imazapyr and phenol, and has been compared to that of the commercially available nonporous Aeroxide TiO_2 P-25. For the imazapyr photodegradation, the newly synthesized mesoporous TiO_2 nanocrystals show an initial degradation rate around 2 times higher than the rate observed with the non-porous Aeroxide TiO_2 P25. The highest photocatalytic activity is observed for the samples calcined at 500 °C followed by those calcined at 800 °C. In contrast to that, a different behavior is found for the photodegradation of phenol. The results indicate that the TiO_2 samples calcined at 500 °C show the highest photocatalytic activity for phenol photodegradation. It is proposed that the behavior of the photocatalysts in term of their photocatalytic efficiency and rate constants varies based on the pollutant type. TiO_2 calcined at 500 °C can be considered as economically more efficient by saving energy through the lower temperature required in the calcination process.

* Corresponding author at: Advanced Materials Department, Central Metallurgical R & D Institute (CMRDI), P.O. Box: 87 Helwan, Cairo 11421, Egypt.
E-mail addresses: adelali141@yahoo.com (A.A. Ismail), bahnemann@iftc.uni-hannover.de (D. Bahnemann).

http://dx.doi.org/10.1016/j.cej.2014.11.075
1385-8947/

1. Introduction

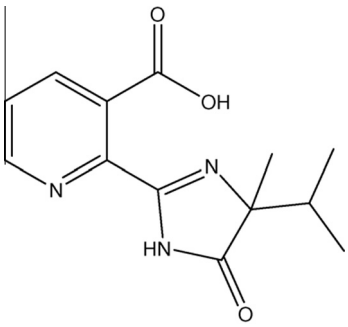
Pesticides and phenol are considered to be the most common type of water and soil pollutants. Imazapyr is a herbicide belonging to the imidazolinone family, which has the ability to damage the plants even at low concentrations [1]. Moreover, imazapyr is a persistent herbicide with a high mobility in soils. The half-life of imazapyr is found to vary from 21 days to 49 months as observed in field studies. Since imazapyr is considered to be groundwater contaminant [1]. Various attempts have been made to remove it from the polluted water using Ozone. However, this process is ineffective since an important amount of imazapyr still remains in the water [2]. Phenols are also highly toxic organic compounds, found in wastewater and effluents coming from the petroleum and chemical industries. Up to now, several studies on the decomposition of imazapyr and phenol using Fenton, photo-Fenton and electro-Fenton processes have been performed [3–6]. This has led to the consideration of heterogeneous photocatalysis as one of the most promising advanced oxidation processes. The interest in this scientific field has increased during the last decades, since photocatalysis is assumed to be a powerful tool for the degradation and remediation of highly toxic pollutants such as imazapyr and phenols.

The photocatalytic oxidation of imazapyr has been performed in the aqueous phase using commercially available Aeroxide TiO_2 P-25, Crystal Global PC-500 [7–9], and PC-500 coated on natural cellulose [10]. However, experimental evidence indicates that mixed phases, such as anatase/rutile [11–13], brookite/rutile [14,15], and brookite/anatase [16–20], exhibit synergistic effects, thus enhancing the photocatalytic activity. The photodegradation of phenol has been extensively studied using TiO_2 [21–23]. Therefore, it is of great importance to develop methods to synthesize TiO_2 with particular properties such as crystal sizes and phases, mesoporous structures and high surface areas and study their influence on the photocatalytic performance. In general, the phase composition and particle size of TiO_2 prepared by wet processes are dependent on the temperature, the pH, as well as on the type and the concentration of the reactants employed in the synthetic reaction [11,24–29]. Mesoporous TiO_2 nanocrystals are promising materials for photocatalytic applications. They have the ability to significantly improve the photocatalytic performance compared to the commercially available P-25 [24–29]. In this work, we report about the synthesis of mesoporous TiO_2 samples and the determination of their respective photocatalytic activity with the respect to the degradation of the two pollutants imazapyr and phenol. We focus on the relationship between the effect of calcination temperature, the phase transformation, and the surface area of the synthesized mesoporous photocatalysts.

2. Experimental section

2.1. Materials

$Ti(OC(CH_3)_3)_4$ (TBOT), HCl, CH_3OH, C_2H_5OH, CH_3COOH, the block copolymer surfactant EO_{106}-$PO_{70}EO_{106}$ (F-127,EO═-CH_2CH_2-O-,PO═-$CH_2(CH_3)$ CHO-, MW 12,600 g/mol), phenol, and Imazapyr ($C_{13}H_{15}N_3O_3$ > 99%) were purchased from Sigma–Aldrich. Scheme 1 shows the chemical structure of the herbicide imazapyr. H_3PO_4 and HCl were purchased from Neva Reactifs Russia, KNO_3 from VEKTON Russia and Methanol from Merck. Aeroxide TiO_2 P-25 from Evonik, (mainly anatase, with a rutile content of ca. 20%, primary particle size of around 30 nm, and BET surface area of this nonporous material of 50 $m^2\,g^{-1}$) was used as received. Water was purified in a Millipore Mill-Q system (resistivity ⩾ 18 MΩ cm).



Scheme 1. Chemical structure of imazapyr.

2.2. Preparation of mesoporous TiO_2

Mesoporous TiO_2 nanocrystals were synthesized through a simple one-step sol–gel process in the presence of the F127 triblock copolymer as the structure directing agent [25,26,30]. In a typical synthesis procedure, 1.6 g of F127 was dissolved in 30 ml of ethanol for 60 min and then added to 2.3 ml of CH_3COOH and 0.74 ml of HCl. Afterwards 3.5 ml of TBOT was gradually added to the mixture. The mixture was stirred vigorously for additional 60 min and transferred into a Petri dish. Ethanol was subsequently evaporated at 40 °C and a relative humidity of 40% for 12 h followed by the transfer of the sample into a 65 °C oven, and the aging for additional 24 h. The as-made hybrid materials were calcined at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C in air for 4 h with a heating rate of 1 °C/min and a cooling rate of 2 °C/min to remove the surfactant and to obtain mesoporous TiO_2 nanocrystals denoted as T-400, T-500, T-600, T-700, and T-800 according to the calcinations temperatures.

2.3. Characterization

X-ray diffraction data were acquired on a Bruker AXS D4 Endeavour X diffractometer using Cu $K\alpha_{1/2}$, $\lambda\alpha_1$ = 154.060 pm, $\lambda\alpha_2$ = 154.439 pm radiation. Transmission electron microscopy (TEM) was performed at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. The nitrogen adsorption and desorption isotherms at −196 °C were determined using a Quantachrome Autosorb 3B. All the samples were vacuum-dried at 200 °C overnight before the measurement. The Barrett–Joyner–Halenda (BJH) model with Halsey equation was employed to analyze the sorption data. Raman spectroscopy was carried out using a Bruker Senterra dispersive Raman microscope. The spectra were taken to the powder samples exposed to air in the range from 0 to 1555 cm^{-1} using a laser excitation wavelength of 532 nm and laser power of 2 mW. Diffuse reflectance spectroscopy (DRS) was employed to measure the bandgap energy of the prepared photocatalysts. A Varian Cary 100 Scan UV-vis system equipped with a Labsphere integrating sphere diffuse reflectance accessory was employed to record the reflectance spectra of the samples at 200–800 nm [31]. The diffuse reflectance mode (R) was transformed to the Kubelka-Munk function $F(R)$ to separate the extent of light absorption from scattering. Furthermore, the band gap values were calculated based on the modified Kubelka–Munk function $(F(R)E)^{1/2}$) and the energy of the absorbed light E as follows in Eq. (1) [32].

$$F(R)E^{1/2} = \left(\frac{(1-R)^2}{2R} \times h\upsilon\right)^{1/2} \quad (1)$$