



Oxidative degradation of phenanthrene in the absence of light irradiation by hybrid ZrO₂-acetylacetonate gel-derived catalyst

Filomena Sannino^a, Domenico Pirozzi^b, Giuseppe Vitiello^{c,d}, Gerardino D'errico^{c,d}, Antonio Aronne^b, Esther Fanelli^b, Pasquale Pernice^{b,*}

^a Università di Napoli Federico II, Dipartimento di Agraria, Via Università 100, I-80055 Portici (Na), Italy

^b Università di Napoli Federico II, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio 80, I-80125 Napoli, Italy

^c Università di Napoli Federico II, Dipartimento di Scienze Chimiche, Complesso Universitario Monte Sant'Angelo, Via Cinthia, I-80126 Napoli, Italy

^d Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Unità di Napoli, Complesso Universitario Monte Sant'Angelo, Via Cinthia, I-80126 Napoli, Italy

ARTICLE INFO

Article history:

Received 25 December 2013

Received in revised form 25 February 2014

Accepted 4 March 2014

Available online 13 March 2014

Keywords:

Acetylacetonate complex

Phenanthrene

ZrO₂ Xerogel

Hybrid material

EPR

ABSTRACT

The intrinsic catalytic activity of a hybrid gel-derived ZrO₂-acetylacetonate (HSGZ) material towards the oxidative degradation of phenanthrene (PHE), in aqueous solution and in the dark, was revealed for the first time.

The HSGZ catalyst is a polymeric network of zirconium oxo-clusters on the surface of which part of Zr⁴⁺ ions are involved in strong complexation with acetylacetonate (*acac*) ligands. The HSGZ gave significant PHE degradation rates acting as radicals initiator without any light irradiation at 30 °C.

Free radicals were formed on the solid surface by the coexistence of Zr(IV)-*acac* and Zr(III)-*acac*^{*} complexes in equilibrium at a given temperature, from which reactive oxygen species were produced in the presence of molecular O₂. A direct evidence of radical's presence on HSGZ solid surface was obtained by EPR spectroscopy.

The analysis of the degradation products confirmed that the reaction goes on through the formation of intermediate free radicals, leading to the first ring-opening and to the formation of phthalates as main intermediates. Subsequently, low molecular weight alkanes are produced. Finally, a deep oxidation of the intermediates occurs completing the mineralization process. The HSGZ catalyst showed a good stability under the reaction conditions, retaining its catalytic activity after repeated tests.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The increase of industrial development, population growth and urbanization has promoted the release of hazardous chemicals in the environment and a general global pollution. Polycyclic aromatic hydrocarbons (PAHs), ubiquitous environmental contaminants found in air, soil and waters, have toxic, genotoxic, carcinogenic and mutagenic effects [1,2]. PAHs exhibit high stability and low water solubility due to the delocalization of π -electrons, leading to their accumulation in food chains, so threatening human health and environment quality [3]. Therefore, the removal of PAHs and the development of effective strategies to remediate polluted sites is a current focus of research in the environmental science.

In the last decades many attempts have been made to remove PAHs from the environment. Traditional chemical or physical technologies, such as sorption [4] or treatment with oxidants [5], have inherent drawbacks due to operating costs, operational problems and production of secondary pollutants [6,7]. On the other hands, the low solubility of these organic compounds hampers the bioremediation techniques [8] such as phytoremediation [9] or biodegradation by fungi or bacteria [5]. To date, the development of an effective method for PAHs degradation still remains a challenge.

In the recent years, photocatalysis by either solar energy or artificial light has emerged as one of the most attractive strategies for PAHs degradation. Heterogeneous photocatalysis offers an oxidative process capable of pollutant removal under ambient conditions via irradiation of some semiconductor solids [10] which can be used as photocatalysts suspended in the water effluent, or immobilized on different types of supports [11]. To date, most of the studies concern TiO₂ [12] due to its stability and its relatively high

* Corresponding author. Tel.: +39 081 7682411; fax: +39 081 7682595.
E-mail address: pernice@unina.it (P. Pernice).

activity, though the band gap of TiO₂ is so large that it can only utilize less than 5% of solar energy. As a result, current interests are directed toward the application of photocatalysts that work under visible light irradiation to efficiently utilize sunlight. Kou et al. [13] showed that the oxidation reactions of five typical PAHs, carried out by using tantalum oxynitride and Pt-tantalum oxynitride, are driven only by the presence of visible radiation, so confirming the great importance of light in this process as reported in the literature [14–16].

In the present paper, we demonstrate for the first time the intrinsic catalytic activity of a gel-derived hybrid zirconia material (HSGZ) toward the phenanthrene (PHE) oxidative degradation in aqueous solution. This catalyst gives high PHE degradation rate acting as a radical initiator without any light irradiation. Phenanthrene is among the 16 PAHs listed as primary pollutants by US Environmental Protection Agency (EPA) [17] and it is known to be a human skin photosensitizer and mild allergen [18]. It is a typical three-ring PAH and has been used as a model compound to test the catalytic activity of HSGZ material in pollutants degradation.

The HSGZ material previously synthesized [19,20] is a class II hybrid ZrO₂-acetylacetonate gel-derived material; after drying at low temperature HSGZ xerogel holds the acetylacetonate used in the sol-gel synthesis and can be considered as an *acac* surface-modified porous zirconia. The catalyst ability to produce free radicals in absence of irradiation has been ascertained by EPR spectroscopy and related to the presence of the *acac* ligands on HSGZ surface. Kinetics of PHE removal was evaluated and a two-steps kinetic model has been proposed.

2. Experimental

Phenanthrene (99.0% purity) was purchased from Sigma-Aldrich (UK). All solvents were of HPLC grade (Carlo Erba, Italy) and were used without further purification.

The hybrid sol-gel zirconia (HSGZ) was prepared according to the procedure elsewhere reported [19]. A solution containing 10 mL of zirconium(IV) propoxide (70 wt.% in 1-propanol) (22.6 mmol), 1.5 mL of acetylacetonate (99+%) (14.6 mmol) and 3.0 mL of 1-propanol (99.80+%) (39.9 mmol) was prepared and stirred at room temperature for a few minutes. A second solution containing 3.0 mL of distilled water (166 mmol) and 5.5 mL of 1-propanol (73.2 mmol) was added to the first one. The solution obtained was vigorously stirred for about 20 min at room temperature, until the gelation occurred. A homogeneous slightly yellow colored gel was obtained. The gel was left at room temperature for 24 h and then lyophilized at -50 °C for 20 h to obtain the porous amorphous material (about 300 m²/g) [21]. A reference ZrO₂ matrix (SGZ) was also prepared in similar conditions except for the lack of acetylacetonate in the solution of the Zr precursor. Consequently, when the hydro-alcoholic solution was added to the precursor solution, the instantaneous formation of a particulate gel took place.

Gel-derived zirconia material, HSGZ, has been characterized by Electron Paramagnetic Resonance (EPR). The powder sample was analyzed using an X-band (9 GHz) Bruker Elexys E-500 spectrometer (Bruker, Rheinstetten, Germany). The capillary containing the sample was placed in a standard 4 mm quartz sample tube. The temperature of the sample was regulated at 25 °C and maintained constant during the measurement by blowing thermostated nitrogen gas through a quartz Dewar. The instrumental settings were as follows: sweep width, 100 G; resolution, 1024 points; modulation frequency, 100 kHz; modulation amplitude, 1.0 G; time constant, 20.5 ms. EPR spectra were measured with attenuation of 10 dB to avoid microwave saturation of resonance absorption curve. Several scans, typically 64, were accumulated to improve the signal-to-noise ratio. The *g* values were evaluated by means of two

internal standards (1,1-diphenyl-2-picrylhydrazyl (DPPH) and a 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) ethanol solution) which were inserted in the quartz sample tube co-axially with the capillary containing the HSGZ sample [22].

A stock aqueous solution of PHE 0.8 mg L⁻¹ was prepared and subsequently it was kept refrigerated in the dark to avoid photocatalytic degradation reactions. Blanks of PHE in aqueous solution were analyzed in order to check its stability and the possible sorption to vials. The PHE removal was studied as a function of the solid/liquid ratio *R* (*R* = mg of matrix/1 mL of PHE aqueous solution). The following ratios were used: *R* = 0.1, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0 and incubation time of 60 min. All the tests were carried out in the dark to avoid any additional photocatalytic degradation. After incubation in a thermostatic rotary shaker at 30 °C, the samples were centrifuged at 10,000 rpm for 10 min and the supernatants were analyzed as described below. The percentage removal of PHE (*X*) was calculated by the following equation:

$$X = \frac{c_0 - c}{c_0} \times 100 \quad (1)$$

where *c*₀ and *c* are the concentrations of PHE (mg L⁻¹) at the start and at the end of the incubation, respectively.

Kinetic tests in the presence of HSGZ matrix at *R* = 0.4 were performed fixing incubation times of 5, 10, 15, 30, 60, 120, 360 and 1440 min at 30 °C.

The long-term applicability of the PHE-removal system was verified by carrying out repeated batch tests at *R* = 10 and after 1 h of incubation time. After each batch test, the liquid phase was removed and replaced by an equal volume of PHE solution at the initial concentration of 0.8 mg L⁻¹.

Analytical determination of PHE was performed by an Agilent 1200 HPLC apparatus (USA), equipped with a DAD and a Chem-Station Agilent Software. A Macharey-Nagel Nucleosil 100-5 C18 column (stainless steel 250 mm × 4 mm) was utilized. The mobile phase, a binary system of 85:15 acetonitrile: water, was pumped at 1 mL min⁻¹ flow in isocratic mode. The detector was set at 252 nm and the injection volume was 20 μL. The quantitative determination of PHE was performed using a calibration curve between 0.05 and 0.8 mg L⁻¹.

The PHE degradation products were extracted and identified by Gas Chromatography-Mass Spectrometry (GC-MS) analysis. In a typical experiment, 5 mL of PHE aqueous solution (0.8 mg L⁻¹) was incubated with 50 mg of HSGZ for 1 and 24 h, respectively. After reaction, the slurry of reaction mixture was taken out and centrifuged to remove the HSGZ solid. The collected supernatants were extracted in a separatory funnel with *n*-hexane in the ratio 1:6 (v:v). This procedure was repeated by three times to assure all of PHE degradation products were extracted. The *n*-hexane layer was dried by anhydrous sodium sulphate, evaporated under reduced pressure at 30 °C and dissolved in 1 mL of dichloromethane phase before GC-MS analysis.

The samples were analyzed using a Perkin-Elmer AutoSystemTM XL gas chromatograph, equipped with a Programmed-Temperature Split/Splitless injector with programmable pneumatic control kept at a constant temperature of 250 °C, a Restek Rtx-5MS capillary column (5% diphenyl-95% dimethylpolysiloxane, length 30 m, 0.25 mm ID, and 0.25 μm df), and a Perkin-Elmer TurboMass Gold mass-spectrometer. The oven temperature was programmed to run at 60 °C for 5 min and then to increase by 15 °C min⁻¹ to a final temperature of 280 °C. Under these conditions the retention time for PHE was 12.75 min. A NIST mass spectral library version 1.7 was used for peak identification. All the experiments were performed in triplicate and the relative standard deviation was lower than 4%.

Download English Version:

<https://daneshyari.com/en/article/6501248>

Download Persian Version:

<https://daneshyari.com/article/6501248>

[Daneshyari.com](https://daneshyari.com)