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Photodeposition of Ni nanoparticles on TiO_2 and their application in the catalytic ozonation of 2,4-dichlorophenoxyacetic acid

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ABSTRACT

Different photochemical approaches have been investigated to prepare supported nickel nanoparticles to be used in the catalytic ozonation of 2,4-dichlorophenoxyacetic acid (2,4-D). Direct photochemical (λ = 365 nm, without TiO_2) and photocatalytic deposition in presence or absence of sensitizers (TiO_2, acetone or benzophenone) were employed. The characterization of the catalysts was carried out by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The photocatalytic deposition without any sensitizer resulted to be the most suitable method to obtain in very short irradiation time, Ni nanoparticles randomly distributed over the support with a particle size ranging from 7 to 15 nm. An optimization of this technique was performed by varying the mass of TiO_2 and the light intensity. According to the results of 2,4-D degradation, the catalytic ozonation with Ni/TiO_2 catalyst presented a slightly higher conversion than TiO_2 or ozonation alone. These results were explained in terms of the two phases (NiO/Ni) present on the surface of TiO_2 which favor the ozone decomposition forming OH radicals useful for 2,4-D degradation. A reaction pathway including all the intermediates formed during the direct attack of ozone and the produced OH radicals was proposed.

1. Introduction

There is a growing need for understanding the mechanisms for catalytic ozonation to introduce this technique in water treatment at industrial scale [1–3]. Current research has been divided into two routes, homogeneous and heterogeneous catalytic ozonation. Concerning the last route, several catalysts have been tested, including metal oxides, metals on supports, minerals and activated carbon, among others [3]. The catalytic ozonation can proceed by direct molecular ozone reactions and by an indirect pathway forming OH radicals after ozone decomposition. However, the ozonation process alone has its limitations, and the most important is that the total mineralization of toxic organic compounds is difficult to achieve. Therefore, the presence of a catalyst in the ozonation process improves and controls the ozone decomposition and OH radicals formation leading to mineralization [3].

In recent years, several researchers have reported on the degradation of organic pollutants by the heterogeneous catalytic ozonation using TiO_2 [4–6], NiO unsupported and supported [7–9] and other metal oxides [10,11], however, a general conclusion about the reactivity with each kind of catalyst is not clear yet. In contrast, supported metal catalysts have been scarcely studied specifically in the effect of the preparation method on the degradation performance. In particular, if supported metal catalysts are employed in the catalytic ozonation of contaminants is thought that two reaction mechanisms can occur. By the first mechanism, organics are adsorbed on the surface of the catalyst and then attacked by ozone or hydroxyl radicals; by the second mechanism, both ozone and organics adsorb on the surface of the catalyst and a redox process takes place forming organic radicals that are subsequently oxidized by hydroxyl radicals or ozone [1,3].

As is well known, the catalyst preparation method plays an important role in the size, morphology and particle size distribution [12]. In fact, during the last two decades, several synthetic methods such as chemical, thermal, photochemical, radiation, among others, have been used in the preparation of metallic or metal oxide nanoparticles [13–16]. According to our previous works, a photodeposition method ensures the formation of small Pt particles (2–4 nm) supported on C or TiO_2 with a narrow particle size distribution [17,18]. In a general way, the photodeposition process takes place when the chromophore of a complex absorbs a photon resulting in a photoexcited state, then, the complex may decompose by a photoredox reaction to produce a solid metallic phase cluster able to deposit over the substrate surface [19–23]. The photodeposition

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method is reproducible and the reaction can be stopped at any time by switching the lamp off. However, byproducts coming from the solvent oxidation/decomposition reactions can be generated after irradiation [24].

Diverse catalysts based on supported nickel have been used in chemical processes industrially important, including hydrogenation, methanation, reforming, dechlorination, desulfurization, and so on. These catalysts are generally synthetized by impregnation or coprecipitation with nickel salts on a support [25]. Nevertheless, it presents the problem of formation of mixed nickel oxides, especially for nickel loadings of 10 wt% and high calcination temperatures (≥600 °C), which are required to completely reduce the Ni(II) cations to metallic nickel particles, which leads to the unwanted metal sintering [26]. Therefore, one of the main advantages of the photodeposition method is the direct reduction of the Ni precursor avoiding reductive thermal treatments. Works devoted to the photodeposition of Ni nanoparticles on semiconductors are scarce and the effect of synthesis parameters has not been reported yet [27].

In this study, we have explored the use of TiO_2 to promote the photocatalytic deposition of Ni nanoparticles. The nickel (II) present in the precursor solution is reduced with the photogenerated electrons on the TiO_2 surface. Additionally, an easily oxidable compound (e.g. ethanol) must be present in the system to assure that holes are consumed to avoid their accumulation on the photocatalyst surface, which could stop the photocatalytic activity or cause nickel reoxidation [28,29]. It seems that the addition of oxalate ion as a co-reactant favors the reduction of nickel (II) on TiO_2 by an indirect photoreduction in aqueous solution [27].

The evaluation of our photodeposited Ni/TiO_2 catalysts was carried out in the degradation of herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) by heterogeneous catalytic ozonation in aqueous solution. 2,4-D was selected as a model compound, since it is the most widely used in agriculture sector and herbicide in the world, it is poorly biodegradable and has been detected as a major pollutant in ground and surface water [30].

2. Experimental

2.1. Materials and reagents

The bis(2,4-pentandionato) Ni(II) (Ni(acac)$_2$, Aldrich) was reagent grade. Anhydrous ethanol and acetone (J.T. Baker) were spectrophotometric grade. TiO_2 powder P25 (Degussa AG, 80% anatase and 20% rutile, non-porous, BET surface area = 44 $m^2\,g^{-1}$) was used as starting material. 2,4-dichlorophenoxyacetic acid (Alfa Aesar, 90%) and benzophenone (Aldrich, analytical grade) were used as received.

2.2. Catalyst preparation

In a glass reactor, it was added a TiO_2 (0.1 g) suspension containing a 8×10^{-4} M alcoholic solution of Ni(acac)$_2$ at 25 °C to have a total volume of 100 mL, purged with nitrogen. The mixture was irradiated with 14 black light UVA lamps (8 W) with a maximum emission at about 365 nm. The sensitized photoreaction was performed in presence of acetone (0.2 M) or benzophenone (10^{-3} M). The suspension was subjected to vigorous and continuous stirring to avoid both the film formation and sedimentation of TiO_2. After irradiation, the sample was dried at 120 °C to evaporate the solvent. The kinetics of the Ni(acac)$_2$ photodecomposition was performed by using a Lambda UV–Vis spectrophotometer (Perkin Elmer) at wavelength of 310 nm.

2.3. Characterization techniques

The specific surface area of the supported catalyst Ni/TiO_2 and the TiO_2 support were determined by the BET method of nitrogen adsorption using a MicromeritisAutochem II 2920. Metal content in the prepared catalyst was obtained using an atomic absorption spectrophotometer (Perkin Elmer). XRD patterns were obtained in a XïPert-P analytical diffractometer with a Cu source ($\lambda K\alpha$ = 0.15418 nm) and operated at 40 kV and 35 mA. The instrument was coupled with a nickel filter and a X'Celerator detector and it was settled in tetha/2tetha configuration. The scanning angle (2θ) range was varied to 20–90° with 0.016 step size and 20 s of counting time. Phase analysis was carried out matching diffracted intensities with PDF cards.

TEM images were obtained using a JEOL-JEM-2200 field emission operated at 200 kV. The samples were prepared with the catalyst (<1 mg) in methanol and dispersed by ultrasound for 5 min. Thereafter, a drop of the solution was placed over a carbon coated Cu grid (300 mesh) and dried at room temperature. Photoelectron core-level spectra of the as-prepared samples were obtained with an X-ray photoelectron spectroscopy (XPS) system (Riber LDM-32), which has an analysis chamber equipped with an ion pump, an electron-energy analyzer (Mac-3) and a dual anode X-ray source. XPS data were collected using the Al Kα line at 1486.6 eV. The high resolution XPS scans were completed at 0.1 eV energy steps and 0.5 eV resolution (~25 eV pass energy), while the surveys at 1 eV steps and 3 eV resolution (~100 eV pass energy). The spectra were decomposed into their components with mixed Gaussian–Lorentzian lines by a non-linear least squares curve-fitting procedure, using the public software package XPSPEAK 4.1. The binding energies and FWHM of the peaks were determined from the fitting results after subtraction of the Shirley-type background. Deconvoluted peak areas and standard sensitivity factors were used to evaluate the surface composition of the samples.

2.4. Ozone generation and ozone consumption control

Ozone was generated from dry oxygen by the ozone generator (corona discharge type) HTU500G (AZCO Industries Limited – Canada). The Ozone Analyzer BMT 964 BT (BMT Messtechnik, Berlin) provides the ozone monitoring in the gas phase at the reactor outlet for the control of the ozonation degree, the ozone consumption and the ozone decomposition as well.

2.5. Ozonation procedure

All experiments with ozone were carried out in a semi-batch type reactor (0.5 L) at 21 °C. The agitation was provided by means of an ozone–oxygen mixture bubbling through a ceramic porous filter, which is placed at the bottom of the reactor. The initial ozone concentration was 25 mg L^{-1}. The ozone–oxygen mixture flow was 0.5 L min^{-1}. A flow diagram showing the ozonation procedure and equipment is depicted in Fig. 1.

The model solution of 2,4-D herbicide was prepared with a concentration of 80 mg L^{-1}. Aliquot of 3-mL ozonation reaction solution was withdrawn at time intervals from the reactor for sequent analysis. The catalyst concentration was 0.1 g L^{-1}.A HPLC apparatus (Perkin-Elmer series 200, UV/Vis detector) was used to record the change of concentration of 2,4-D, under the following operation conditions: column Prevail Organic Acid 5 μ "Grace", 150 × 4.6 mm with 60:40 acetonitrile–buffer mobile phase of KH_2PO_4 at 25 mM adjusted a pH 2.6 with H_3PO_4 at wavelength 225 nm with the flow 1 mL min^{-1}.