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Nitric oxide removal by action of ZnO photocatalyst hydrothermally synthesized in presence of EDTA

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ABSTRACT

ZnO samples with different morphologies were synthesized in presence of ethylenediaminetetraacetic acid disodium salt (EDTA) at 200 °C under hydrothermal treatment. The morphology of the nanostructures obtained was modified by changing the concentration of EDTA and the reaction time. The effect of the reaction conditions on the morphology, crystallization as well as in the optical and textural properties of the ZnO samples was investigated by using scanning electron microscopy (SEM), X-ray powder diffraction (XRD), UV–Vis absorption spectroscopy (DRS) and adsorption-desorption N_2 isotherms (BET). The ZnO performance as photocatalyst was evaluated in the oxidation reaction of nitric oxide (NO) under UV irradiation. The study revealed that ZnO samples with morphology of nanoplates showed significantly higher NO removal than other ZnO samples with morphologies of rods and flower-type. The ZnO sample with the highest photocatalytic activity was measurement using different mass and its stability was tested after several photocatalytic cycles. By the use of scavenger species was determined the participation mainly of the superoxide anion ($O_2^{\cdot-}$) and holes (h^+) in the photocatalytic oxidation process of NO.

1. Introduction

The air pollution is one of the major problems facing many big cities around the world [1]. Taking into account that half of the world population is concentrated in the big cities, a high percentage of the people in the earth has a poor quality in the air that breathes [2]. The main pollutants in the air are the suspended solid particles (PM), nitrogen oxides (NO_x), sulfur dioxide (SO_2), tropospheric ozone (O_3), carbon monoxide (CO), volatile organic compounds (VOCs) and some simple aromatic hydrocarbons [3,4]. The emission sources of these pollutants are varied, but the most important are the high concentration of automobiles in the big cities and the burning of fossil fuels by the industrial activity. The nitrogen oxides (NO_x = NO + NO_2) are one type of air pollutants with harmful incidence in the human health and the environment. For example, these types of compounds have been associated with affections of the cardiovascular and respiratory systems. In the same way, NO_x gases travel long distances from their source of generation to react with other compounds of the atmosphere to form acid rain, ozone (O_3), and photochemical smog [5,6]. There are numerous studies that relate the high concentrations of this type of substances with severe diseases and even with high incidence of mortality [7,8].

Nowadays, different technologies for the control of NO_x emissions have been developed. However these techniques are not sufficient to control the presence of the pollutants at low concentrations and cannot be used in all cases with the same efficiency [9]. Therefore, recent works are focusing on the search for effective methods to reduce the concentration of NO_x gases in the atmosphere. The heterogeneous photocatalysis is a promising technology that has gained great attention over the two past decades since it offers excellent prospects to the control of the environmental pollution [10]. This technology is based on the use of a semiconductor which can be activated under UV or visible irradiation to photocatalyze reactions that involves the decomposition of pollutants presents in air or water. For this purpose, several semiconductor materials have been investigated for test their performance as photocatalysts. Among them, ZnO is recognized as a suitable material due to its non-toxicity, high photosensitivity, high redox potential, natural abundance and relative low cost. In the same way, the ZnO system is characterized by a great variety of morphologies in function of the synthesis route followed [11,12]. This feature is important because the photocatalytic properties of ZnO are strongly dependent of the morphology and the preferential crystalline orientation of its particles [13,14]. Among the synthetic methods, the hydrothermal route is the most used due to the control in the size and morphology of the synthetized particles [15]. Nevertheless, the growth of particles with different morphologies depends of the preferential orientation of

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Table 1
Previous works where ZnO was tested as photocatalyst in the oxidation reaction of NO_x gases.

Synthesis	Reagents	Morphology	BET area ($m^2\ g^{-1}$)[a]	NO conversion degree (%)[b]	Ref.
Precipitation/structrural agents	$Zn(NO_3)_2{\cdot}6H_2O$ $(CH_2)_6N_4$ C_2H_7NO	Spindle, sunflower, dandelion, and disk	39	55	[19]
Solvothermal	$Zn(NO_3)_2{\cdot}6H_2O$ $(CH_2)_6N_4$ $Na_3C_6H_5O_7$	Spheres	607	70	[20]
Hydrothermal method/ ionic liquid.	$Zn(O_2CCH_3)_2$ NaOH $[TBA]_2$[L-Tar].	Roses	33	20	[21]
Precipitation/hydrothermal/ sol-gel method.	$Zn(NO_3)_2{\cdot}6H_2O$ $Zn(O_2CCH_3)_2$ NH_4OH	Agglomerates and bars	16	70	[13]
Sol-gel	$Zn(O_2CCH_3)_2{\cdot}2H_2O$ NH_4OH	Bars, semispherical and flake-like	30	75	[14]
Sol-gel/liquid ionic	$Zn(O_2CCH_3)_2$ $\{[CH_2CH_2]\ O_2\ (mm)_2\}$	Hexagonal mesoporus plates	84	80	[22]

[a] Maximum surface area.
[b] Maximum NO conversion degree reached.

certain crystalline planes during their growing, frequently influenced by the use of chelating agents as it can be seen in previous works. For example, Zhang et al. [16] prepared flower-type ZnO nanostructures by hydrothermal process using cetyltrimethylammonium bromide (CTAB). Adhyapak et al. [17] reported also the synthesis of flower-type ZnO nanostructures through hydrothermal reaction using polyethylene glycol (PEG) as surfactant with application as photocatalyst for the degradation of methylene blue. In the same way, Ram et al. [18] obtained nanorods-bunch, hexagonal nanorods and flower-type particles of ZnO by hydrothermal method using EDTA as chelating agent. The study of ZnO as photocatalyst in the oxidation reaction of NO_x is limited, as can be seen from the few works reported in the literature (see Table 1). In general, the nitric oxide conversion degrees has not reached more than 80% when ZnO synthesized in presence of complex structuring agents was used as photocatalyst.

In this work, the effect of EDTA as retarder agent in the formation of particles of ZnO will be analyzed. The synthesis route proposes the use of EDTA instead of the use of complex agents of high cost. The effect of some experimental conditions such as EDTA concentration and reaction time on the final physical properties ZnO will be also investigated. The ZnO samples will be tested as photocatalyst in the oxidation reaction of the nitric oxide (NO). In the same way, some aspects of the photocatalytic mechanism will be evaluated by the use of scavenger agents of high energy species.

2. Experimental

2.1. Synthesis of ZnO

The chemical reagents zinc acetate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$, DEQ. 99.5%), potassium hydroxide (KOH, DEQ. 87.13%) and ethylenediaminetetraacetic acid disodium salt (EDTA, DEQ) were analytic grade and were used without further purification. The synthesis of ZnO was realized by hydrothermal method through a typical procedure as described below. Initially 0.01 mol of zinc acetate were dissolved in 100 mL of deionized water under continuous stirring to form a clear solution (Solution A). After, three solutions of EDTA in deionized water were prepared with concentrations enough to reach a molar ratio Zn:EDTA of 1:0.1, 1:0.3 and 1:0.5 (Solution B). Additionally, a solution of 0.1 mol of KOH in 100 mL of deionized water (Solution C) was prepared. Then, the solution A was dropping to the solution B with continuous stirring. After this process the solution C was added. Once these solutions were mixed, the resulting solution was immediately transferred to a hydrothermal reactor where it was heated at 200 °C for 0.1, 1 and 4 h, respectively. The white precipitate obtained was filtered and washed several times with deionized water and ethanol. Finally, the precipitate was dried at 70 °C in air for 24 h.

2.2. Characterization

The structural characterization of ZnO samples was carried out by X-ray powder diffraction in a Bruker D8 Advance diffractometer with CuK_α radiation and Ni filter. The microstructure of the samples was analyzed in a FEI NOVA NanoSEM 200 scanning electron microscope. The optical absorbance of samples was measured by diffuse-reflectance spectroscopy (DRS) in an Agilent Cary 4500 Series spectrophotometer and the energy band gap was calculated through the Kubelka-Munk function. The specific surface area was determined in accordance with the Brunauer-Emmett-Teller (BET) method in a Bel-Japan Minisorp II analyzer. The samples were also analyzed by Fourier transform infrared spectroscopy (FTIR) by using a FTIR AFFINITY-1S Shimadzu spectrophotometer to identify reaction byproducts.

2.3. Photocatalytic activity

The experimental tests for the nitric oxide removal were performed in a stainless steel continuous flow reactor with a volume of 0.8 L designed with the requirements established in ISO 22197-1. For this purpose, 50 mg of the ZnO photocatalyst were dispersed in ethanol and then applied onto the glass substrate by the help of a brush covering thus an area of 0.08 m^2. A mixture of 3 ppm of NO stabilized in N_2 was used as inlet gas. The concentration of inlet gas was diluted to 1 ppm in NO by using synthetic air (20.5 vol% O_2 and 79.5 vol% N_2) and the flow rate of gas was adjusted to 1 L min^{-1}. Three 20 W fluorescent lamps with a maximum emission at 365 nm were used as source of UV irradiation. The outlet NO concentration was continuously measured using an EcoPhysics CLD88p chemiluminescence detector. The concentration of NO_2 was determined by the difference in the concentration between NO_x (NO_x = NO + NO_2) and NO using an EcoPhysics PC860 photolytic converter. The NO conversion degree was calculated for each time following the Eq. (1):

$$\text{NO conversion degree} = \frac{NO_i - NO_f}{NO_i} x \quad 100 \tag{1}$$

where $[NO]_i$ is the initial concentration of nitric oxide, and $[NO]_f$ is the nitric oxide concentration in the semi steady-state of the system for different times of lamp irradiation.

A series of experiments were performed with the purpose to identify the role of the high energy species in the photocatalytic process as well as establish a possible mechanism for the oxidation of NO. Several