



Tungstophosphoric acid immobilized on ammonium Y and ZSM5 zeolites: Synthesis, characterization and catalytic evaluation

Candelaria Leal Marchena^{a,c}, Romina A. Frenzel^{b,c}, Silvina Gomez^{a,c}, Liliana B. Pierella^{a,c,**}, Luis R. Pizzio^{b,c,*}

^a Grupo Zeolitas – CITEQ (Centro de Investigación y Tecnología Química), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro Lopez esq Cruz Roja Argentina, 5016 Córdoba, Argentina

^b Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. J.J. Ronco” (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No. 257, 1900 La Plata, Argentina

^c Conicet (Consejo Nacional de Investigaciones Científicas y Técnicas), Argentina

ARTICLE INFO

Article history:

Received 6 September 2012

Received in revised form 29 October 2012

Accepted 3 November 2012

Available online 14 November 2012

Keywords:

Tungstophosphoric acid

Zeolites

4-Chlorophenol

Photocatalytic degradation

ABSTRACT

Two series of materials based on tungstophosphoric acid (TPA) immobilized on NH₄Y and NH₄ZSM5 zeolites were prepared by wet impregnation of the zeolite matrix with TPA aqueous solutions. Their concentration was varied in order to obtain TPA contents of 5, 10, 20 and 30% (w/w) in the solid. The materials were characterized by N₂ adsorption–desorption isotherms, XRD, FT-IR, ³¹P MAS-NMR, TGA-DSC, DRS–UV–vis, and the acidic behavior was studied by potentiometric titration with n-butylamine.

The specific surface area (S_{BET}) decreased when the TPA content was raised as a result of the zeolite pore blocking. The X-ray diffraction patterns of the solids modified with TPA only presented the characteristic peaks of NH₄Y and NH₄ZSM5 zeolites, and an additional set of peaks assigned to the presence of (NH₄)₃PW₁₂O₄₀. According to the Fourier transform infrared and ³¹P magic angle spinning–nuclear magnetic resonance spectra, the main species present in the samples (except for NH₄YTPA05) is the [PW₁₂O₄₀]³⁻ anion, which was partially transformed into [P₂W₂₁O₇₁]⁶⁻ anion during the synthesis and drying steps. The thermal stability of the NH₄YTPA and NH₄ZSM5TPA materials is similar to that of their parent zeolites. Moreover, the samples with the higher TPA content present band gap energy values similar to those reported for TiO₂.

The immobilization of TPA on NH₄Y and NH₄ZSM5 zeolites is a good method to obtain catalysts with high photocatalytic activity in the 4-chlorophenol degradation. They can be reused at least three times without an important decrease in the degradation degrees.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The degradation of chemicals present in wastes by heterogeneous photocatalysis is an important issue and its study is a constantly growing field. An increasing number of papers deal with TiO₂ (titania) as one of the most appropriate semiconductor materials to be employed as a photocatalyst, due to its high activity in

the photodegradation of organic compounds, low cost, low toxicity, and chemical stability [1–8].

It is generally reported that titania performance in the photodegradation of contaminants contained in wastes is influenced by the crystal structure, crystallinity, surface area, porosity, and band gap energy [9–11], among other factors.

The low surface area and the fast recombination of the photoinduced electrons and holes are the main effects that can lead to a low photocatalytic activity. Transition metals or metal oxides were used as electron trappers to avoid the recombination of the electron–hole pairs of TiO₂-based catalysts [12–15], improving the photocatalytic activity.

Moreover, different heteropolyoxometalates (POM) have been added to titania suspensions [16] or anchored to TiO₂ by chemical interactions [17], incorporated either into titania colloids [18] or into the TiO₂ matrix during the titania gel synthesis [19–21] with the purpose of reducing the charge recombination in UV-illuminated TiO₂. The capacity of heteropolyoxometalates

* Corresponding author at: Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. J.J. Ronco” (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No. 257, 1900 La Plata, Argentina. Fax: +54 221 425 4477.

** Co-corresponding author at: Grupo Zeolitas – CITEQ (Centro de Investigación y Tecnología Química), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro Lopez esq Cruz Roja Argentina, 5016 Córdoba, Argentina.

E-mail addresses: lpierella@scdt.frc.utn.edu.ar (L.B. Pierella), lrpizzio@quimica.unlp.edu.ar (L.R. Pizzio).

as acceptors of the electrons of UV-irradiated titania suspensions, generated in the conduction band (e_{cb}^-) together with holes in the valence band (h_{vb}^+), was demonstrated by Park and Choi [22] using a photoelectrochemical method.

POM are widely used as oxidation as well as acid catalysts [23–25]. They are also employed as effective homogeneous photocatalysts in the degradation of organic pollutants in water [26–29].

Heteropolyoxometalates absorb strongly in the near visible and UV region of the light spectrum ($\lambda < 400$ nm). This absorption corresponds to the ligand-to-metal charge-transfer band and it can generate strongly oxidizing excited state POM* (reaction (1)). They are able to carry out the oxidation of organic substrates (S) (reaction (2)) directly via charge transfer or H-atom abstraction, or indirectly through the intermediacy of solvent-derived radicals [29]. After that, the corresponding reduced POM are usually reoxidized to their original oxidation state by an electron acceptor such as dioxygen (reaction (3)).



The studies on the photocatalytic behavior of POM have been performed mainly on bulk acids and their salts, though, from a practical point of view, supported systems are more interesting. Some of the major drawbacks of POM as catalysts are related to their high solubility in oxygenated solvents and their relatively low specific surface area [23]. Supporting the POM on solids with high surface area is a useful method for improving catalytic performance in liquid–solid and gas–solid heterogeneous reactions. It has been reported that among other factors, the catalytic activity of POM-supported catalyst depends on the support type, the concentration and nature of the chemical species present, and their degree of interaction with the support [20,23]. Silica and NaY zeolite were employed to prepare promising heterogeneous POM-based photocatalysts [30]. According to Ozer and Ferry [30] the use of zeolites as support enhances the “local concentration” of the oxidizable substrate and also the stabilization of charge-transfer state and transient species such as $\bullet\text{OH}$.

Y and ZSM-5 zeolites, with uniform pore size and high specific surface area, are considered as good materials to support and stabilize POM [31–34].

In the present work, we attempted to combine the well-known photocatalytic properties of tungstophosphoric acid, one of the most widely employed POM in homogeneous photocatalysis, and the above-mentioned properties of zeolites as POM supports to synthesize heterogeneous photocatalytic materials.

They were prepared by impregnation of tungstophosphoric acid onto two different zeolites (NH_4Y and $\text{NH}_4\text{ZSM5}$) with the aim of studying their influence on the physicochemical and textural characteristics of the solids, and to discuss the effect of the preparation variables on 4-chlorophenol degradation. The photocatalytic degradation of 4-CP has been investigated by many research groups and has become a standard reaction for evaluating various experimental parameters in photocatalysis. To the best of our knowledge, this is the first time that these materials have been successfully synthesized and tested in the photodegradation of this pollutant.

2. Experimental

2.1. Sample preparation

Zeolite NH_4Y ($\text{Si}/\text{Al} = 2.47$) was provided by Aldrich. ZSM5 material ($\text{Si}/\text{Al} = 17$) was obtained by the hydrothermal crystallization method. An aqueous solution of sodium aluminate was added to a

silica solution that was previously prepared by partial dissolution of tetrapropylammonium hydroxide (TPAOH) in water. The obtained gel reached a $\text{pH} > 9$ and was maintained at 120–160 °C for 12–16 days under self-generated pressure on autoclave. Afterwards, reaction products were extracted, washed and dried at 110 °C for 12 h. The structure-directing agent (TPAOH) was desorbed in N_2 atmosphere (20 ml/min) at programmed temperature (10 K/min) from 110 to 520 °C and then it was calcined in air at 520 °C for 12 h to obtain Na-HZSM5. The ammonium form of the material ($\text{NH}_4\text{ZSM5}$) was prepared by ion exchange of NaZSM5 with a NH_4Cl solution (1 M) for 40 h at 80 °C [35].

The tungstophosphoric acid (TPA) solutions were prepared from $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 23\text{H}_2\text{O}$ (Fluka p.a.) using distilled water as solvent. The incorporation of TPA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) onto the zeolite matrix was realized by wet impregnation in a rotary evaporator at 80 °C. The amount of TPA to be deposited onto the surface of the zeolite was varied with the purpose of obtaining a TPA concentration of 5%, 10%, 20% and 30% by weight in the final solids that, for zeolite NH_4Y , were named $\text{NH}_4\text{YTPA05}$, $\text{NH}_4\text{YTPA10}$, $\text{NH}_4\text{YTPA20}$ and $\text{NH}_4\text{YTPA30}$, respectively; and for zeolite $\text{NH}_4\text{ZSM5}$, $\text{NH}_4\text{ZSM5TPA05}$, $\text{NH}_4\text{ZSM5TPA10}$, $\text{NH}_4\text{ZSM5TPA20}$ and $\text{NH}_4\text{ZSM5TPA30}$, respectively. The solids were dried under vacuum at 80 °C.

2.2. Sample characterization

2.2.1. Textural properties

The specific surface area and the mean pore diameter of the solids were determined from the N_2 adsorption–desorption isotherms at the liquid-nitrogen temperature, obtained using Micromeritics PulseChemisorb 2700 equipment. The solids were previously degassed at 100 °C for 2 h.

2.2.2. Nuclear magnetic resonance spectroscopy

The ^{31}P magic angle spinning-nuclear magnetic resonance (^{31}P MAS-NMR) spectra were recorded with Bruker Avance II equipment, using the CP/MAS ^1H – ^{31}P technique. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5 μs pulses, a repetition time of 4 s, and working at a frequency of 121.496 MHz for ^{31}P at room temperature. The spin rate was 8 kHz and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

2.2.3. Fourier transform infrared spectroscopy

The Fourier transform infrared FT-IR spectra of the solids were obtained using a JASCO 5300 spectrometer and pellets in KBr in the 400–4000 cm^{-1} wavenumber range.

2.2.4. X-ray diffraction

The X-ray diffraction (XRD) patterns were recorded with Philips PW-3020 equipment with a built-in recorder, using $\text{CuK}\alpha$ radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5° and 50° 2θ at a scanning rate of 2° per min.

2.2.5. Thermogravimetric analysis and differential scanning calorimetry

The TGA-DSC measurements of the solids were carried out using a Shimadzu DT 50 thermal analyzer. The thermogravimetric and differential scanning calorimetry analyses were performed under argon or nitrogen, respectively, using 20–30 mg samples and a heating rate of 10 °C/min. The studied temperature range was 20–700 °C.

Download English Version:

<https://daneshyari.com/en/article/45830>

Download Persian Version:

<https://daneshyari.com/article/45830>

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