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Valorization of biomass derivatives: Keggin heteropolyacids supported on titania as catalysts in the suitable synthesis of 2-phenoxyethyl-2-furoate

Angélica M. Escobar Caicedo[a], Julián A. Rengifo-Herrera[a,*], Pierre Florian[c], Mirta N. Blanco[a], Gustavo P. Romanelli[a,b,**], Luis R. Pizzio[a]

[a] 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, Buenos Aires, Argentina
[b] Cátedra de Química Orgánica, CISAV, Facultad de Ciencias Agrarias y Forestales, UNLP, Argentina
[c] CNRS, CEMHTI UPR3079, Université d'Orléans, F-45071 Orléans, France

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ABSTRACT

Titania modified by tungstophosphoric (TPA) and tungstosilicic (TSA) acid (30% w/w) were synthesized by the sol-gel method, using urea as low cost pore-forming agent and annealing at 500 °C for 2 h (TiO_2/TPA and TiO_2/TSA respectively). The obtained materials were characterized by ^{31}P, ^{29}Si, ^{1}H nuclear magnetic resonance (^{31}P, ^{29}Si, ^{1}H MAS-NMR), X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), Raman spectroscopy (FT-Raman), acid strength by potentiometric titration with *n*-butylamine. Mesoporous materials were obtained, without important microporosity, as determined from N_2 adsorption-desorption isotherms by the Brunauer-Emmett-Teller (BET) method. The XRD patterns of the modified samples exhibited only peaks of anatase phase. According $^{31}P/^{29}Si$ MAS-NMR and XPS studies, the main species present in the TiO_2/TPA and TiO_2/TSA samples are the Keggin anions by forming surface acid species, and probably surface complex between Keggin anion and titania as well. Solids were evaluated in the synthesis of 2-phenoxyethyl-2-furoate, by esterification of 2-furoic acid, a valuable product which can be obtained from biomass, with 2-phenoxyethanol, where TiO_2/TPA sample showed the highest catalytic activity. The reaction temperature, molar ratio acid:alcohol and catalyst amount were studied as variables using TiO_2/TPA sample. Results of catalytic activity and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT-FT-IR) measurements suggested that the reaction mechanism may involve a protonated intermediate of 2-furoic acid polarizing the C=O bond of the acid, and leaving that can be easily attacked by 2-phenoxyethanol.

1. Introduction

High Brönsted acidity, thermal stability, low volatility, fast and reversible redox multielectronic transformations in mild conditions, lead to the heteropolyacids (HPAs), such as tungstophosphoric (TPA) and tungstosilicic (TSA) acids, suitable features as catalysts participating in different organic reactions [1,2]. However, these compounds present two important drawbacks to overcome: (i) their low surface area and (ii) the solubility in polar media, which limit their use as heterogeneous catalysts [2]. In order to overcome these problems, the HPAs have been supported on different substrates such as silica, titania, activated carbon, zirconia among others [3–8].

On the other hand, the esterification is one of the most important reactions in drug synthesis and the organic esters are important products and/or intermediates in the industrial production of fragrances, flavorings, polymers, polyesters, plasticizers, fatty acids, biofuels and paints [9]. For these reasons, the searching of novel, clean and sustainable methodologies for esters synthesis is a very important issue [10]. Solvent-free reactions have advantages as pollution reduction by organic solvents, and low costs due to the less use of reactive and process simplification by decreasing steps,

* Corresponding author.
** 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, Buenos Aires, Argentina.
E-mail addresses: julianregifo@quimica.unlp.edu.ar (J.A. Rengifo-Herrera), gpr@quimica.unlp.edu.ar (G.P. Romanelli).

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such as removal of the solvent, which are important factors in the industry [11]. Esters are often synthesized by condensation reactions between carboxylic acids and alcohols using sulfuric acid, *p*-toluenesulfonic acid or phosphoric acid, all toxic and corrosive acids [12].

The esterification of several acids such as formic [13], oleic [14], acetic acid [6] using supported tungstophosphoric acid on zirconia and silica has already been reported on the literature, where capital parameters such as acid:alcohol ratio, catalyst amount, reaction temperature and catalyst recycle have been highlighted.

Furoic acid is a promising product in biomass valorization since it can be used as intermediate in pharmaceutical, food, cosmetics and perfumery industries [15]. This acid is produced from lignocellulosic material which comes from agricultural or forestry wastes [16].

In a previous study recently reported by some of us, TPA supported on zirconia was used as catalyst in esterification of 2-furoic acid with different alcohols [17]. Esterification reaction of 2-fuoric acid with 2-phenoxyethanol in the presence of TPA-zirconia catalysts led to the formation of 2-phenoxyethyl-2-furoate (estimated by GC–MS) and it was also found that parameters such as 2-fuoric acid:alcohol molar ratio and reaction temperature played an important role.

The aim of this study was to synthesize and characterize by multitechniques two catalysts based on tungstophosphoric and tungstosilicic acid supported on titania, studying the stability of immobilized TPA and TSA by XPS, $^{31}P/^{29}Si$ MAS NMR, FT-Raman. On the other hand, the acidity and the presence of acid sites were studied by potentiometric titration and ^{1}H MAS-NMR, respectively. Furthermore, it was evaluated their catalytic activity in the esterification of 2-furoic acid with 2-phenoxyethanol, taking into account variables such as temperature, acid-alcohol ratio and catalyst amount. Finally, the product 2-phenoxyethyl-2-furoate was analyzed by ^{1}H and ^{13}C NMR in order to confirm its presence.

2. Experimental section

2.1. Materials

The chemical substances used to synthesize the TiO_2-based samples and photocatalytic tests were: titanium tetraipropoxide (99% Sigma-Aldrich), urea (99% Sigma-Aldrich), tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}23H_2O$) and tungstosilicic acid ($H_4SiW_{12}O_{40}{\cdot}23H_2O$) (99% Fluka), furoic acid (99% Sigma-Aldrich), 2-phenoxyethanol (99% Fluka), ethanol (Merck grade absolute), HCl (37% Carlo Erba). All chemicals were used as received.

2.2. Samples preparation

Titanium isopropoxide (26.7 g) was mixed with absolute ethanol (186.6 g) and stirred for 10 min to obtain a homogeneous solution under N_2 at room temperature, then 0.33 mL of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction and was left for 3 h. Then 120 g of urea–alcohol–water (1:5:1 wt ratio) solution was added to the hydrolyzed solution under vigorous stirring, to act as template, together with an ethanol solution of $H_3PW_{12}O_{40}{\cdot}23H_2O$ (TPA) or $H_4SiW_{12}O_{40}{\cdot}23H_2O$ (TSA). The amount of TPA or TSA solutions was fixed in order to obtain a concentration of 30% TPA or TSA (w/w).

The xerogels were dried at room temperature in a beaker. The solids were ground into powder and extracted with distilled water for three periods of 24 h to remove urea, in a system with continuous stirring. Finally, the solids were thermally treated at 500 °C for 2 h. The samples will be named TiO_2-TPA and TiO_2-TSA, respectively.

The TPA and TSA content on the TiO_2/TPA and TiO_2/TSA samples were estimated as the difference between the W amount contained in the heteropolyacid solution originally used for the impregnation and the amount of W in the water solutions obtained after the solid washing (in order to remove the urea). The W content was determined by atomic absorption spectrometry using a Varian AA Model 240 spectro-photometer as it was already reported in a previous study [18]. The calibration curve method was used with standards prepared in the laboratory. The analyses were carried out at a wavelength of 254.9 nm, bandwidth 0.3 nm, lamp current 15 mA, phototube amplification 800 V, burner height 4 mm, and acetylene–nitrous oxide flame (11:14).

2.3. Samples characterization

2.3.1. Nuclear magnetic resonance spectroscopy (NMR)

^{29}Si and ^{31}P MAS-NMR experiments were performed on a 9.4 T Avance Bruker Spectrometer operating at 161.9 MHz and 79.5 MHz respectively. It was used a 4 mm diameter rotor spinning at 10 kHz and applied a Bloch decay (single pulse acquisition) with a radio-frequency field of 100 kHz (^{31}P) and 35 kHz (^{29}Si) and pulse width of 10°. Due to the very small amount of NMR active nuclei in the sample, no relaxation time measurement could be performed and it was chosen a recycle delay of 15 s (^{31}P) and 1s (^{29}Si) based on various trials while accumulating between 21120 (3.7 days) and 642600 (7.5 days) scans, respectively. ^{1}H MAS-NMR experiments were performed on a 17.6 T Avance III Bruker spectrometer operating at 750.3 MHz. Hahn echo experiments were performed spinning at 30 kHz to remove the large probe background using a delay of 5 rotor periods (160 μs) and a radio-frequency field strength of 100 kHz. ^{31}P spectra have been referenced to a 1 M solution of H_3PO_4, whereas ^{29}Si and ^{1}H ones have been referenced to tetramethylsilane.

2.3.2. Fourier transform raman spectroscopy (FT-Raman)

Raman scattering spectra were recorded on a Raman Horiba Jobin-Yvon T 64000 instrument with an Ar+ laser source of 488 nm wavelength in a macroscopic configuration.

2.3.3. Acid strength by potentiometric titration

The solid (0.05 g) was suspended in acetonitrile (Merck) and stirred for 3 h. Then, the suspension was titrated with 0.05 N n-butylamine (Carlo Erba) in acetonitrile using Metrohm 794 Basic Titrino apparatus with a double junction electrode.

2.3.4. Atomic absorption spectrometry (AAS)

Tungsten (W) determination was carried out using an atomic absorption spectrometer Varian AA model 240 spectrophotometer. Calibration method was used with in house prepared standards. Analysis were carried out at a wavelength of 254.9 nm, bandwidth 0.3 nm, lamp current 15 mA, phototube amplification 800 V, burner height 4 mm, and acetylene-nitrous (11:4).

2.3.5. Diffuse reflectance fourier transform infrared spectroscopy (DRIFT-FTIR)

FTIR spectra were recorded on a FT-IR Perkin-Elmer Frontier instrument equipped with a DRIFT (Perkin Elmer) accessory. Spectra were recorded using 1024 scans having a resolution of 4 cm^{-1}.

2.3.6. X- ray photoelectron spectroscopy (XPS)

XPS analyses were carried out with XPS Analyzer Kratos model Axis Ultra with a monochromatic AlKα and charge neutralizer. The deconvolution software program was provided by Kratos, the manufacturer of the XPS instrument. All the binding energies were referred to the C1s peak at 285 eV of adventitious carbon. Powder