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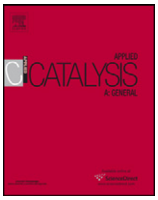

Tungstophosphoric acid/zirconia composites prepared by the sol–gel method: An efficient and recyclable green catalyst for the one-pot synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes

Toa S. Rivera, Alexis Sosa, Gustavo P. Romanelli, Mirta N. Blanco, Luis R. Pizzio*

Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No 257, B1900AJK La Plata, Argentina

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ABSTRACT

Samples of zirconia modified with different contents of tungstophosphoric acid (TPA) were synthesized from zirconium propoxide via sol–gel reactions using polyethylene glycol as template and were characterized by different physicochemical techniques (BET, XRD, FT-IR, and ^{31}P MAS-NMR). The S_{BET} of the solids decreases and the microporosity increases with the increase of the TPA content. According to FT-IR and ^{31}P MAS-NMR studies, the main species present in the samples is $[PW_{12}O_{40}]^{3-}$ anion, which was partially transformed into $[P_2W_{21}O_{71}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ anions during the synthesis and drying steps. The XRD patterns of the modified samples exhibit neither the characteristic peaks of TPA nor those attributed to its decomposition products.

Aryl-14*H*-dibenzo[*a*,*j*]xanthenes have been synthesized by a one-pot condensation of 2-naphthol and aryl aldehydes, catalyzed by tungstophosphoric acid/zirconia composites in a solvent-free medium using conventional heating. The present approach offers the advantages of clean reaction, simple methodology, short reaction time, and high yield. The reaction work-up is very simple and the catalyst can be easily separated from the reaction mixture and reused several times in subsequent reactions without appreciable loss of the catalytic activity.

1. Introduction

Organic reactions catalyzed by inorganic solid materials are gaining much importance due to the advantages of heterogeneous catalysis, such as simplified product isolation, mild reaction conditions, easy recovery and catalyst reuse, and reduction of waste by-products [1–3].

In particular, catalysis by heteropolyacids (HPA) and related compounds is a field of increasing significance worldwide. Many developments have been carried out both in basic research and in fine chemistry processes [4]. HPA have been used as valuable and versatile acid catalysts for some acid-catalyzed reactions because of their strong acidic properties [5,6]. They can be used as bulk or supported materials in both homogeneous and heterogeneous systems. Furthermore, HPA have several advantages, such as much flexibility in the modification of the acid strength, ease of handling, nontoxicity and environmental compatibility [7].

Zirconium oxide (zirconia) is an interesting material to be used as catalyst support due to its thermal stability, and its basic and acid properties. The latter can be modified by the addition of cationic or anionic substances. For example, the addition of sulfate or tungstate ions has been widely studied, obtaining materials with high acidity [8,9]. However, the addition of Keggin heteropolyacids has not been studied so much [10–14]. The most common methods to obtain zirconia are: sol–gel, micellar or mechanochemical synthesis [15]. The preparation of HPA supported on zirconia employing the micellar method, with zirconyl chloride as oxide precursor, has been more extensively reported than the sol–gel method using a zirconium alkoxide [13]. In addition, different types of ionic and neutral surfactants have been employed to obtain mesoporous materials with high specific surface area. More recently, nonsurfactant, low-cost organic compounds, such as urea, have started to be used as pore-forming agents [16].

Conversely, the preparation of organic compounds involving greener processes under solvent-free conditions has been investigated worldwide due to stringent environmental regulations. The implementation of several transformations in a single operation is highly compatible with the principles of Green Chemistry [17–19].

Xanthenes and benzoxanthenes are interesting compounds for the pharmaceutical industry due to their wide range of biological and therapeutic properties [20], such as anti-inflammatory, antibacterial, antiviral, and stimulating activity of the central

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* Corresponding author. Fax: +54 221 4211353.
E-mail address: lrpizzio@quimica.unlp.edu.ar (L.R. Pizzio).

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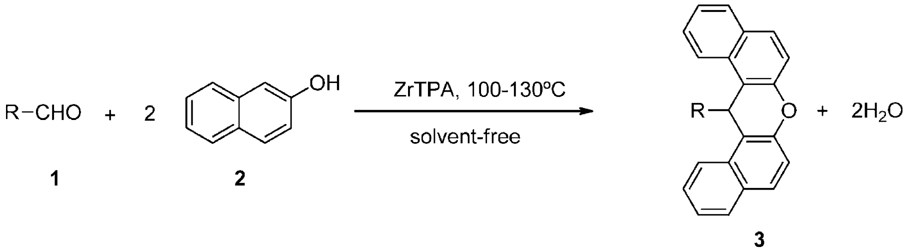

Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes with TPA/zirconia composites as catalyst.

nervous system [21–24]; they are also used in photodynamic therapy [25] and for antagonism of the paralyzing action of zoxazolamine [26].

Different routes have been reported for the synthesis of xanthenes and benzoxanthenes, such as the reaction of aryl oxomagnesium halides with triethylorthoformate, trapping of benzynes by phenols, cyclization of polycyclic aryltriflate esters, and cyclocondensation between 2-hydroxy aromatic aldehydes and tetralone [27–30]. However, one of the best routes is the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes from 2-naphthol and aldehydes in the presence of a catalyst [31] such as AcOH-H_2SO_4, *p*-TSA, Amberlist-15, silica-sulfuric acid, and bulk or silica-supported heteropolyacids [32–37].

But, although these methods showed different degrees of success, some of them had limitations, such as large reaction times, low yields, use of toxic solvents, and harsh reaction conditions [37,38]; that is why the development of alternative clean procedures for the synthesis of benzoxanthenes and related compounds is a challenge. In this regard, our research group has experience in the friendly synthesis of heterocyclic compounds using HPA, such as coumarins, dihydropyrimidinones, azlactones, and flavones [39–42].

Continuing with the studies directed toward the development of highly expedient methods and the synthesis of diverse heterocyclic compounds, we are herein reporting a new one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes from aldehydes and 2-naphthol under solvent-free conditions (Scheme 1), catalyzed by tungstophosphoric acid-modified mesoporous zirconia obtained from zirconium propoxide as precursor and polyethylene glycol as pore-forming agent.

2. Experimental

2.1. Catalyst preparation

Zirconium propoxide (Aldrich, 26.6 g) was mixed with absolute ethanol (Merck, 336.1 g) and stirred for 10 min to obtain a homogeneous solution under N_2 at room temperature. Then 0.47 cm^3 of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction.

After 3 h, an appropriate amount of polyethylene glycol (PEG)–alcohol–water solution (1:5:1 weight ratio) was added to the hydrolyzed solution under vigorous stirring to act as template. The amount of added solution was fixed in order to obtain a template concentration of 10% by weight in the final material. A tungstophosphoric acid $H_3PW_{12}O_{40}\cdot 6H_2O$ (TPA) solution, whose concentration was varied in order to obtain a TPA concentration of 30% and 60% w/w in the solid, was added together with the template addition (ZrTPA30B and ZrTPA60B samples) and also after 24 h of the gel aging (ZrTPA30A and ZrTPA60A samples). A sample without TPA addition was obtained with the aforementioned procedure (ZrTPA00A).

The gels were then kept in a beaker at room temperature up to dryness. The solids were ground into powder and extracted with distilled water for three periods of 8 h, in a system with continuous stirring, to remove PEG. Afterwards, the solids were calcined at 100 °C for 24 h.

2.2. Catalyst characterization

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 ASAP 2020 equipment. The solids were previously degassed at 100 °C for 2 h.

The X-ray diffraction (XRD) patterns were recorded with Philips PW-1732 equipment with a built-in recorder, using Cu Kα radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5° and 60° 2θ at a scanning rate of 1° per min.

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.

The Fourier transform infrared (FT-IR) spectra of the solids were obtained using a Bruker IFS 66 FT-IR spectrometer and pellets in KBr in the 400–4000 cm^{-1} wavenumber range.

The acidity of the solids was estimated by means of potentiometric titration. A known mass of solid was suspended in acetonitrile and stirred for 3 h. Then, the suspension was titrated with 0.05 N n-butylamine in acetonitrile using Metrohm 794 Basic Titrino apparatus with a double junction electrode.

2.3. Synthesis of aryl-14H-dibenzo[a,j]xanthenes

All chemical reagents were obtained from Aldrich and were used without further purification. All products were identified by comparison of their physical and spectral data with those of the authentic samples. Melting points were measured using a Bioamerican Bs 448 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Varian 200 MHz (see Supplementary data). The purity of the substances and the progress of the reaction were monitored by TLC on silica gel, and yields refer to isolated products.

A mixture of the aldehyde (1.2 mmol), 2-naphthol (2 mmol) and the catalyst (50 mg TPA) was stirred at 130 °C for the desired time. The reaction mixture was cooled to 25 °C, then toluene (5 cm^3) was added, and the mixture was stirred for 15 min before being filtered to separate the catalyst. It was washed twice with toluene (3 cm^3). The combined toluene extracts were washed twice with water (5 cm^3), dried over anhydrous Na_2SO_4 and evaporated in vacuo. The obtained solid was recrystallized from ethyl alcohol to afford the pure 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivative.