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12-Tungstophosphoric acid supported on zirconia as an efficient and heterogeneous catalyst for the synthesis of bis(indolyl)methanes and tris(indolyl)methanes

Jitendra R. Satam, Kalpesh D. Parghi, Radha V. Jayaram *

Department of Chemistry, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400 019, India

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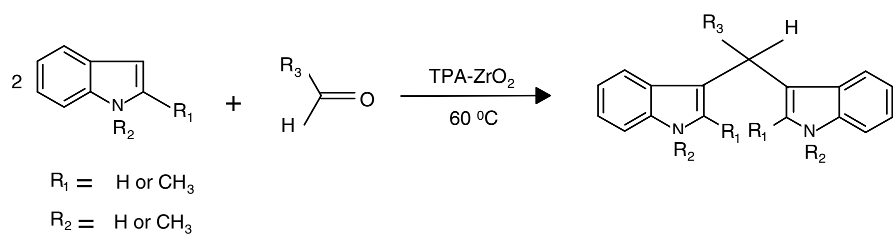
Abstract

12-Tungstophosphoric acid (TPA) supported on zirconia was employed as an efficient, heterogeneous catalyst for the liquid phase electrophilic substitution reactions of indoles with aldehydes or indole aldehyde to afford the corresponding bis(indolyl)methanes or tris(indolyl)methanes in good to high yields. The catalytic efficiency of TPA was found to increase after supporting on zirconia, which was expressed in terms of TON (turnover number) and TOF (turnover frequency, h^{-1}). The catalyst was characterized by XRD, FTIR, BET surface area, elemental analysis and SEM technique and was found to be reusable without significant loss of activity.



Keywords: 12-Tungtophosphoric acid; Bis(indolyl)methane; Tris(indolyl)methane; TON

1. Introduction

The synthesis and the reactions of indoles have received much attention as a number of their derivatives find applications in the field of pharmaceuticals, agrochemicals and material sciences [1–3]. The substrates including bis(indolyl)methane moieties such as secondary metabolites [4] and marine sponge alkaloids [5,6] are of remarkable significance. Three-substituted indoles are versatile intermediates for the synthesis of a wide range of indole compounds [7,8]. One of the simple and direct methods for the synthesis of three-substituted indoles is by the reaction of two equivalents of indole with the carbonyl group. The acid-catalyzed condensations of indole with carbonyl compounds have been of concern as a useful route for preparation of bis(indolyl)methanes. The protic acids [9–11], and Lewis acids [12–15], have been used in excess and drastic conditions. To abate the environmental pollution of the disposal of the excess acids and improvement of the condensation reactions of indole and carbonyl compounds, a number of catalytic systems such as $NaHSO_4/SiO_2$ [16], Zeolites [17,18], ionic liquids [19,20], I_2 [21] and $LiClO_4$ [22] have been successfully utilized. Alternative

* Corresponding author. Tel./fax:+91 22 24145616.
E-mail address: jiten_uict@yahoo.co.in (R.V. Jayaram).

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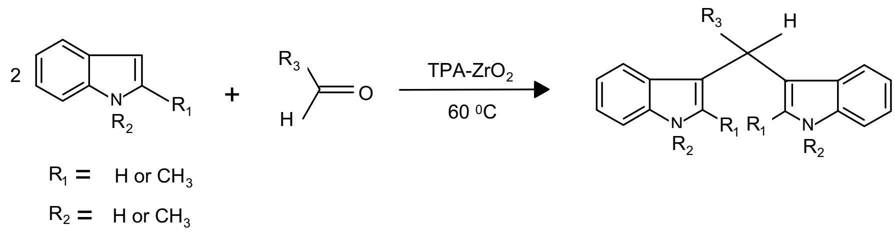

Scheme 1.

catalytic protocols promoted by solid Lewis and Bronsted acids such as montmorillonite clay [23–25], have received an attention, especially for industrial requirements. The use of rare earth catalysts such as $In(OTf)_3$, $La(OTf)_3$, $La(PFO)_3$ [26,27] have been also reported for the promotion of this reaction. Solvent-free condensation of indoles with carbonyl compounds is scarce in the literature [28]. Herein, we report 12-tungstophosphoric acid supported on zirconia as an efficient catalytic system for the carbon–carbon bond formation between indoles and aldehydes under solvent-free conditions in good yields (Scheme 1). 12-Tungstophpsphoric acid (TPA) supported on zirconia is a water-tolerant and reusable catalyst and was prepared as per standard procedure [29,30].

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was prepared by hydrolysis of zirconium oxychloride (0.5 M) by the dropwise addition of aqueous NH_3 (10 M) to a final pH of 10.0. The precipitate was filtered and washed with deionized water until it was free from chloride ions as determined by the silver nitrate test. Zirconium hydroxide thus obtained was dried at 120 °C for 12 h, powdered well and dried for another 12 h. A series of catalysts with different TPA loadings (5–20%) were prepared using a methanolic solution of TPA. 4 mL of methanol was used per g of solid support. The mixture was stirred for 4 h. After stirring, the excess of methanol was removed at 50 °C under vacuum. The resulting solid materials were dried at 120 °C for 24 h and ground well. The dried samples were then calcined in air at 600 °C. These catalysts were named as 5-ZTPA, 10-ZTPA, 15-ZTPA and 20-ZTPA as per the TPA loadings.

2.2. Catalyst characterization

The elemental compositions of W and P in the catalysts were determined by ICP-AES spectrometry. Surface area measurements were carried out by nitrogen adsorption on a Micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatised Cu Kα radiation. The FTIR spectra were recorded on a Perkin–Elmer (Spectra 100) spectrometer. Scanning electron micrographs were obtained on a LEO 440 instrument (20 kV) with carbon coating.

2.3. General procedure for the preparation of bis(indolyl)methanes

A mixture of an aldehyde (2 mmol), indole (4 mmol) and 15-ZTPA (0.25 mol%) was stirred at 60 °C for the appropriate reaction time (Table 2). After complete conversion as indicated by TLC, acetone (10 ml) was added to the reaction mixture and the catalyst was filtered. Evaporation of the solvent under vacuum afforded a crude product which was purified by a column chromatography eluted with ethyl acetate/petroleum ether to give the desired product in high yields. The products were identified by melting point, IR and ^{1}H NMR spectroscopic data.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. X-ray diffraction

XRD spectrum of unsupported TPA exhibits characteristic peaks ($2\theta = 10°$ and $28°$). In case of TPA supported on zirconia these peaks were found to retain. It was observed that the pure zirconia contains tetragonal as well as monoclinic phases with the latter as the major constituents. For catalyst prepared with low TPA loading, the XRD pattern can be described as the sum of monoclinic and tetragonal phases of zirconia. As the amount of TPA increases, it shows increase in the tetragonal phase which enhances the catalytic performance [31]. Fifteen weight percent of TPA supported on zirconia (15-ZPTA) is showing completely tetragonal form of zirconia (Fig. 1). This is due to monolayer coverage of TPA over zirconia. But on further increase in TPA loading, i.e. for 20 wt% ZPTA, it shows monoclinic along with tetragonal phase.

3.1.2. IR spectra of the catalysts

FTIR spectra were recorded for the confirmation of the stabilization of Keggin structure on the surface of zirconia (Fig. 2). TPA exhibits three major bands at 1070, 981 and 890 cm^{-1} which are assigned to stretching absorption modes of oxygen atom bonded to tungsten and phosphorous (W–O), (P–O) and (W–O–W), respectively of the Keggin ion $[PW_{12}O_{40}]^{3-}$. The FTIR spectra of 15-ZPTA (Fig. 2b) shows bands at 1072, 966 and 870 cm^{-1}, which