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ORIGINAL ARTICLE

Sulfated zirconia as an efficient heterogeneous and reusable catalyst for one pot synthesis of flavanones

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Abstract A simple and one pot process for the synthesis of flavanones in the presence of SO_4^{2-}/ZrO_2, a reusable, heterogeneous catalyst has been described. The reactions were conducted both with and without solvent (using toluene as solvent) at 140 °C with reaction times of 3–4 h. Under these conditions several examples were found with very good yields (73–87%) and up to 83% selectivity. The catalyst was easily recycled and reused without loss of its catalytic activity. The present synthetic method is a simple, clean and environment friendly alternative for synthesizing substituted flavanones.

1. Introduction

The flavanones are a class of naturally occurring polyphenolic compounds which are extensively distributed in vascular plants (Lee et al., 2007). These are minor ingredients of the human diet, (Kabalka and Mereddy, 2005; Bennardi et al., 2007) the most abundant being the flavanones. Members of this class have been shown to display a wide variety of biological activities, (Viuda-Martoz et al., 2008) such as antioxidant effect, inhibition of HIV-1 proteinase, and anticancer (Yanling et al., 2007), vasodilator, antiviral and antiallergenic (Alan and Miller, 1996), in addition to antimicrobial (Cushnie and Lamb, 2005; Young et al., 2007), anti-inflammatory (Pan et al., 2010) activities. The curiosity in the biological properties of flavanones has resulted extreme synthetic efforts toward the synthesis of different flavanones. There are number of methods available for the synthesis of flavanones and their analogs. The general methods to obtain flavanones are the cyclization of 1,3-diphenylpropane-1, 3-diones or *o*-hydroxychalcones (Lee et al., 2007; Pathak et al., 2008) and Baker and Venkataraman rearrangement wherein *o*-hydroxyacetophenone is benzoylated to form the benzoyl ester (Diana et al., 2000;

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Balogh and Laszlo, 1993; Chisem et al., 1997). Other methods include Allan–Robinson synthesis and intramolecular Wittig strategy (Huang et al., 2003; Ganguly et al., 2005). But these methods are not environment friendly because of using homogeneous catalysts, such as $FeCl_3$ (Kumar and Perumal, 2007), sodium acetate (Wu et al., 1989), H_2SO_4 (Zembower and Zhang, 1998), Palladium–Thiourea (Miao and Yang, 2000), SeO_2 (Ballesteros et al., 1995), acetic acid (Kalinin et al., 1990), DMSO (Makrandi and Kumari, 1989; Agrawal and Soni, 2005) $NiCl_2$/Zn/KI (Miyake et al., 2003), $Br_2/CHCl_3$, NaOAc/AcOH, EtOH/HCl, clay (Varma et al., 1998). Chemical and pharmaceutical industries are always in search of environment friendly methodologies for organic transformations. To overcome these problems different solid acid catalysts, such as zeolites, clays, Al-MCM-41, oxides like alumina (Varma et al., 1985), magnesium oxide (Drexler and Amiridis, 2003), and supported reagents like supported trifluoromethanesulfonic acid have been used in this transformation (Parvulescu et al., 2005). These heterogeneous catalysts are not only recyclable and easier to separate from the reaction mixture, but also show better selectivity than homogeneous catalysts. However most of them require tedious preparation methods and the use of expensive and toxic solvents (Wang et al., 2005; Drexler and Amiridis, 2003). It is known that sulfated zirconia an extraordinarily acidic material that exhibits greater catalytic activity than that of 100% sulfuric acid in several catalytic reactions (Reddy et al., 2006) is an efficient catalyst for different functional group transformations under heterogeneous conditions and has received much attention in organic synthesis (Singh et al., 2011). But nobody has reported this catalyst for the synthesis of flavanones to the best of our knowledge. So herein we report the catalytic efficiency of sulfated zirconia for one pot synthesis of flavanones from substituted benzaldehydes and substituted 2-hydroxyacetophenones (Scheme 1).

2. Experimental

2.1. Catalyst preparation

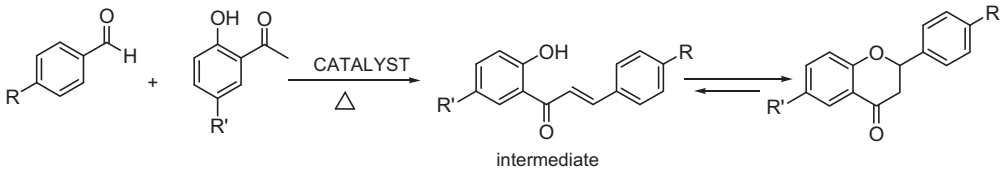
Zirconium oxychloride $ZrOCl_2{\cdot}8H_2O$ (Loba Chemie), ammonia (25 wt%) (Loba Chemie), ammonium sulfate $(NH_4)_2SO_4$ (Loba Chemie), and sodium sulfate Na_2SO_4 (Loba Chemie) were of analytical grade. About 25 g of $ZrOCl_2{\cdot}8H_2O$ was dissolved in 500 ml double distilled water. To this clear solution, dilute aqueous ammonia was added drop-wise from a burette with vigorous stirring until the pH of the solution reached 7.5–8. The gel mixture was stirred continuously for 30 min and the resulting gel was washed with distilled water until free from chloride ions and dried at 120 °C for 24 h. To a fine powder of zirconium hydroxide calculated amount of ammonium sulfate was introduced by implementing the impregnation method. The product was dried at 95 °C and calcined at 550 °C in air atmosphere and stored in vacuum desiccator.

2.2. Catalyst characterization

The surface and bulk properties of zirconia and sulfated zirconia catalyst were examined by different techniques namely X-ray powder diffraction (Fig. 1) BET surface area and ammonia-TPD reported elsewhere (Singh et al., 2011). XRD patterns were recorded at room temperature on a D8 ADVANCE (BRUKER AXS, Germany) diffractometer using CuKα (λ = 0.15418 nm) parallel beam (Gobel Mirror) radiation which illustrates that the catalysts include two types of zirconia phases (ZrO_2) namely tetragonal phases and monoclinic phases (beddeleyite). Crystallite sizes of tetragonal and monoclinic phases are determined using (1 1 1) planes at 2θ value of 30.283° and 28.175°, respectively. The acidity of catalyst was determined by CHEMBET-3000 TPR/TPD/TPO instrument, containing a quartz reactor (i.d. = 4 mm) and a T.C.D. detector. Prior to TPD studies; sample was pretreated at 250 °C for 2 h with continuous flow of pure nitrogen (99.9%) then cooled to room temperature. After pretreatment, the sample was saturated with 10% anhydrous ammonia gas until saturated adsorption. The temperature was increased to 80 °C and kept there for 2 h to remove the physisorbed ammonia. Finally the system was heated from 80 to 1200 °C at the rate of 10 °C/min and the desorbed gas was monitored with a T.C.D. detector. All the flow rates were maintained at normal temperature and pressure (NTP). All the chemicals used in this synthesis of flavanones were purchased from Sigma Aldrich; the procedure for the catalytic reactions was followed from those earlier reported (Wang et al., 2005).

2.3. Reaction in toluene as solvent

In a typical experiment flavanone synthesis was carried out under N_2 in a round bottomed flask equipped with a reflux condenser immersed in a thermostatted bath and stirred magnetically. Model flavanone was prepared by mixing in 15 mmol of benzaldehyde derivative and 10 mmol of substituted *o*-hydroxyacetophenone and heated to 140 °C, 5 ml toluene and SO_4^{2-}/ZrO_2 catalyst (1% mmol) was refluxed with stirring for the indicated time (see Table 1). The reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and washed twice with toluene then with dichloromethane and recycled. The extracts were combined and washed with 1 M NaOH, then with H_2O, and dried with anhydrous sodium sulfate. The



Scheme 1