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Short Communication

Sulfonated rice husk ash (RHA-SO_3H): A highly powerful and efficient solid acid catalyst for the chemoselective preparation and deprotection of 1,1-diacetates

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ABSTRACT

Rice husk ash (RHA), as a source of amorphous silica, was treated with chlorosulfonic acid and sulfonated rice husk ash (RHA-SO_3H) as a highly powerful solid acid catalyst was obtained and characterized with a variety of techniques including IR, TGA, SEM, XRD, pH analysis, Hammett acidity function and BET method. This solid acid showed excellent catalytic activity for the protection and deprotection of aldehydes with Ac_2O at room temperature under solvent free conditions. The procedure gave the products in excellent yields in very short reaction times and good to high yields. Also this catalyst can be reused for several times without loss of its catalytic activity.

1. Introduction

Protection and deprotection of functional groups are often necessary during a multistep organic synthesis in order to obtain chemoselectivity. Aldehydes are often present in organic molecules so development of economical, efficient and mild procedures for the protection of them is very important for synthetic organic chemistry. Among various procedures for protection of aldehyde, preparation of 1,1-diacetates from the reaction of aldehydes and acetic anhydride is the most common route due to the stability of the products in the neutral and basic conditions [1,2]. 1,1-Diacetates are also important for the preparation of other compounds, for example in reaction with appropriate nucleophiles they can be converted to other useful functional groups [3]. On the other hand α,β-unsaturated diacetates are important starting materials for Diels–Alder reactions [4]. A variety of catalysts including $FeCl_3$ [2], sulfuric acid [5], Zn-montmorillonite [6], $Bi(NO_3)_3\cdot 5H_2O$ [7], $In(OTf)_3$ [8], P_2O_5/Al_2O [9], $CuSO_4\cdot 5H_2O$ [10], Silica sulfuric acid [11], $HClO_4$-SiO_2 [12], $Al(HSO_4)_3$ [13], SO_4^{2-}/SnO_2 [14], [Hmim]HSO_4 [15] and [bmpy]HSO_4 ionic liquid [16], silica-bonded S-sulfonic acid [17], saccharin sulfonic acid [18], *N*-sulfonic acid poly(4-vinylpyridinium) chloride [19], ZSM-5-SO_3H [20] have been reported for the promotion of the acetylation of aldehydes with acetic anhydride. Although these methods are an improvement, most of them suffer from disadvantages such as long reaction times, need of organic solvents, expensive catalyst, use of excess amounts of the acylating agents, harsh reaction conditions and non-recoverability of the catalyst. Therefore, introduction of efficient and economical catalysts that solve these drawbacks is desirable.

Replacement of conventional, toxic and polluting Bronsted and Lewis acid catalysts with eco-friendly reusable heterogeneous catalysts is an area of current interest. In this context, there has been renewed interest in the synthesis of solid acid catalysts for organic reactions. Solid acid catalysts have many advantages compared to traditional liquid acids such as their efficiency, operational simplicity, easy recyclability and recoverability, non-corrosive nature and friendly to the environment, all factors which are important in industry. Therefore, solid acid catalysts can play a significant role in the development of clean technologies. Among various supports that can be used for the preparation of the above mentioned catalysts (silica, montmorillonite, organic polymer and zeolite), silica is one of the more extensively used cases, because it has many advantages such as ease of handling, commercially available, low cost, high mechanical and thermal stability and non-corrosiveness.

Recently utilization of waste materials has been found to be of increasing interest. Rice husk, the outer covering of rice grains obtained during the milling process, is one of the main agricultural residues. It mainly consists of cellulose, hemicelluloses, lignin, silica and minor other mineral composition [21]. Societies often dispose of the rice husk waste using open burning that leads to environmental pollution and damages to the land and the surrounding area in which it was dumped. In recent years, the application of rice husk as an energy

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source for biomass power plants, rice mills and brick factories is increasing due to its high calorific power [22]. In this combustion, rice husk ash (RHA) is produced. RHA possesses excellent pozzolanic activity due to its high surface area and high silica content [23,24], so it is used in cement, concrete and white ware production and the preparation of lightweight aggregate [25,26]. Also, it has been employed as adsorbent for heavy metals, purifying biodiesel and producing zeolites and silica powders [27–29]. Although useful, the reported method for the preparation of pure silica from rice husk ash needs various stages and a long time [29]. On the basis of these points it can be concluded that, at the same conditions, the use of RHA as a support for the preparation of catalysts is better than the use of silica which is prepared via precipitation method during various stages and long time.

2. Experimental

2.1. Instrumentation

The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on a Bruker Avance DPX-400 FT-NMR spectrometer (δ in ppm). The chemical composition of RHA was analyzed using X-ray fluorescence (XRF) spectrometer (Model Magix Pro, Philips). The FT-IR spectra were run on a VERTEX 70 Brucker company (Germany). Thermogravimetric analyses (TGA) were performed on Polymer Laboratories PL–TGA thermal analysis instrument (England). Samples were heated from 25 to 600 °C at ramp 10 °C/min under N_2 atm. The adsorption–desorption isotherms and the specific surface area (S_{BET}) were determined from nitrogen adsorption studies using Micro neotype StarII system. Scanning electron microphotographs (SEM) were obtained on a SEM-Philips XL30. X-ray diffraction (XRD) measurements were performed at room temperature on diffractometer Model XRD 6000, PHILIPS Xpert pro using Co–Kα radiation (K = 1.7890 Å) with the beam voltage and a beam current of 40 kV and 30 mA, respectively.

2.2. Preparation and chemical composition of RHA

The rice husk sample was obtained from an Iranian type of rice, named as Hassani. It was burned at 600 °C for 1 h to obtain RHA. The X-ray fluorescence (XRF) analysis showed a high value of silica content for the sample (up to 80%). Other composition such as Al_2O_3, Fe_2O_3, SO_3, P_2O_5, K_2O, Na_2O and CaO are also present in RHA as a very small proportion of metallic elements (Table 1).

2.3. Catalyst preparation (RHA-SO_3H)

A 50 mL suction flask charged with 3.0 g of RHA and 10 mL $CHCl_3$, was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (0.7 mL) and a gas inlet tube for conducting HCl gas into water as an adsorbing solution. Chlorosulfonic acid was added drop wise over a period of 20 min while the reaction mixture was stirred in an ice bath (0 °C). After addition was completed the mixture was stirred for an additional 2 h at room temperature to remove HCl. Then, the mixture was filtered and the filtrate was washed with methanol (20 mL) to remove the remaining HCl and the solid residue was dried at 70 °C for 1 h to afford RHA-SO_3H (3.6 g) as an earthy powder (Scheme 1).

Table 1
Chemical composition of RHA conducted by X-ray fluorescence analysis (wt%).

SiO_2	Al_2O_3	Fe_2O_3	SO_3	P_2O_5	K_2O	Na_2O	CaO	Cl	LOI[a]
80.82	0.25	0.38	0.39	0.44	1.25	0.96	0.82	1.99	12.70

[a] Loss on ignition.

Scheme 1. Preparation of the catalyst (RHA-SO3H) catalyzed by RHA-SO3H.

2.4. General procedure for the preparation of 1,1-diacetate

Aldehyde (1 mmol) was added to a mixture of RHA-SO_3H (10 mg) and acetic anhydride (1.5 mmol) and the resulting mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), dichloromethane (20 mL) was added and the catalyst was separated by filtration. The organic phase was washed with 10% aqueous solution of sodium bicarbonate (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the desired product. The solid crude product was purified by recrystallization from cyclohexane. The spectral (IR, ^{1}H and ^{13}C NMR) data of fluorene-3-carbaldehyde as a new compound is presented below:

Table 3, Entry 20: IR (neat) $\nu = 1765$ cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.17$ (s, 6H, CH_3), 2.95 (S, 2H, CH_2), 7.35–7.84 (m, 8H, ArH, CH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 20.9$, 36.9, 90.1, 119.9, 120.2, 123.4, 125.1, 125.5, 126.9, 127.2, 133.7, 140.9, 143.3, 143.5, 143.6, 168.9 ppm.

2.5. General procedure for the deprotection of 1,1-diacetates

A mixture of 1,1-diacetate (1 mmol), RHA-SO_3H (30 mg) in acetonitrile (2 mL) was stirred vigorously at 60 °C. After completion of the reaction (monitored by TLC), the organic solvent was evaporated. Then the reaction mixture was diluted by ethyl acetate (20 mL) and filtered to separate the catalyst. The organic phase was washed with 10% aqueous solution of sodium bicarbonate (2 × 10 mL) to remove excess of Ac_2O and dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The resultant product was passed through a short column of silica gel (n-hexane-EtOAc, 9:1) to afford the pure aldehyde.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. FT-IR analysis

The infrared spectra of RHA and RHA-SO_3H are shown in Fig. 1. In the case of RHA, the peaks at 3460 and 1640 cm ^{1} are respectively

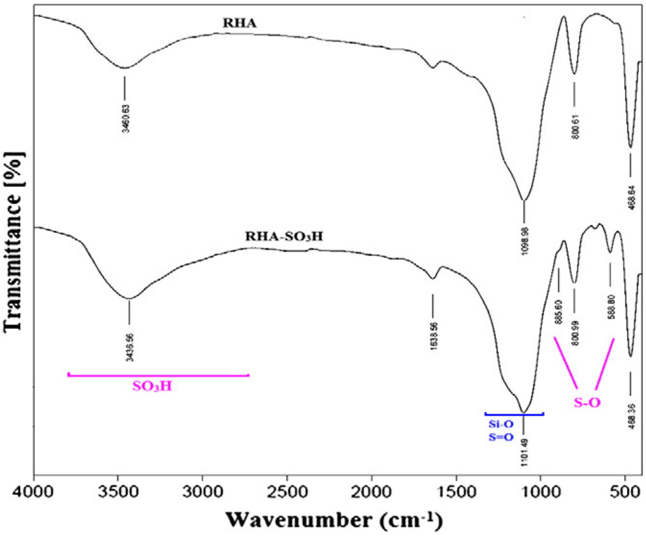

Fig. 1. FT-IR spectra of RHA and RHA-SO_3H.