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Application of rice husk and rice husk ash in organic reactions

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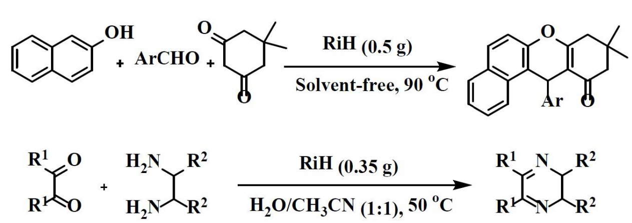
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

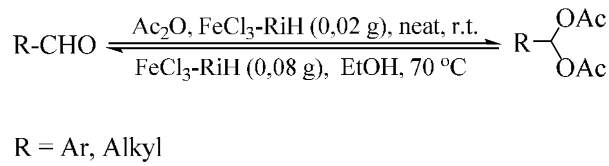
Rice husk (RH), the outer covering of rice grains that obtained during the milling process, is one of the main agricultural residues. It mainly consists of cellulose, hemicelluloses, lignin, silica and minor other mineral composition [1]. Societies often dispose of the rice husk waste using open burning that leads to environmental pollution and damages to the land and the surrounding area in which it was dumped. Application of rice husk as an energy source for biomass power plants, rice mills and brick factories is increasing due to its high calorific power [2]. In this combustion, rice husk ash (RHA) is produced. RHA has a light weight, therefore, the disposal of bulky RHA could be a problem. RHA contains considerable amount of amorphous silica up to 80% and small proportion of impurities such as K_2O, Na_2O and Fe_2O_3 [3]. Therefore, RHA possesses high silica content, so it has been employed to produce zeolites and silica powders [4-5]. In the course of decades, rice husk has found different applications in chemistry and industry. In this respect, it is known that RH and RHA, and amorphous silica obtained from rice husk ash could be used as catalyst or support in organic reactions.

Abstracts

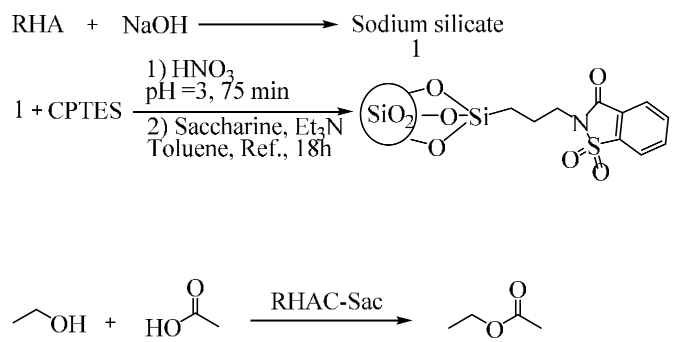
(A) Application of rice husk as catalyst for the promotion of the synthesis of 12-aryl -8, 9,10,12-tetrahydrobenzo[a] xanthen-11-one and quinoxaline derivatives, is the first report on the application of rice husk in the promotion of the organic reactions [6]. The procedure gave the products in excellent yields within very short reaction times under mild and green conditions. Low cost and availability of the catalyst are other advantages of these procedures. Also this catalyst can be reused several times without appreciable loss of its catalytic activity.



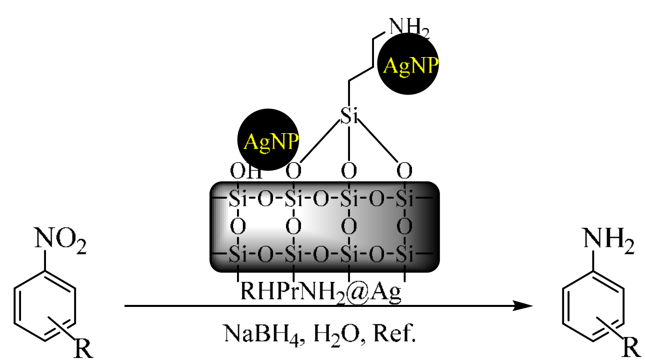
(B) Rice husk supported $FeCl_3$ nanoparticles ($FeCl_3$-RiH) reported by Shirini et al. was used as an efficient and heterogeneous catalyst for the chemoselective protection of aldehydes as their corresponding 1,1-diacetates from the reaction of aldehydes with acetic anhydride [7]. Deprotection of the resulting 1,1-diacetates was also achieved using the same catalyst in ethanol. The catalysts need no regeneration and could be reused four times for the preparation and deprotection of 1,1-diactates without significant loss of activity.



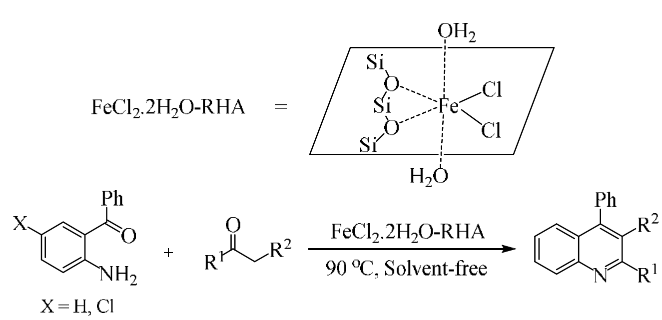
(C) Adam and co-workers have been published several papers on the application of the modified amorphous silica obtained from rice husk ash as catalyst [8-10]. They were immobilized saccharine (Sac) onto rice husk ash (RHA) silica *via* 3-(chloropropyl)triethoxysilane (CPTES) to form a new catalyst, RHAC-Sac. The saccharine loading on the silica was found to be ca. 82%. RHAC-Sac was used as a catalyst in the esterification reaction between ethyl alcohol and acetic acid [8]. A 66% conversion was achieved at 85 ˚C with 100% selectivity for the ester. RHAC-Sac could be reused several times by regenerating at 150 ˚C.



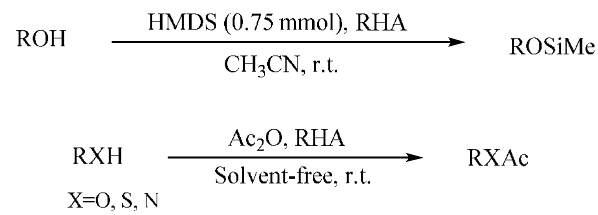
(D) Nanosilica extracted from rice husk ash were modified with aminopropyltrimethoxysilane using sol-gel method. Then, the rice husk propylamine composite ($RHPrNH_2$) was used as a support for the stabilization of silver nanoparticles [11]. Kiasat and Davarpanah were investigated the catalytic activity of $RHPrNH_2$@Ag nanocomposite for the reduction of nitroarenes to the corresponding amines by using $NaBH_4$ as reducing agent in water. In this condition, reduction of different nitroarenes carrying activated and deactivated groups were successfully carried out in 40-75 min with 85-100 % yield.



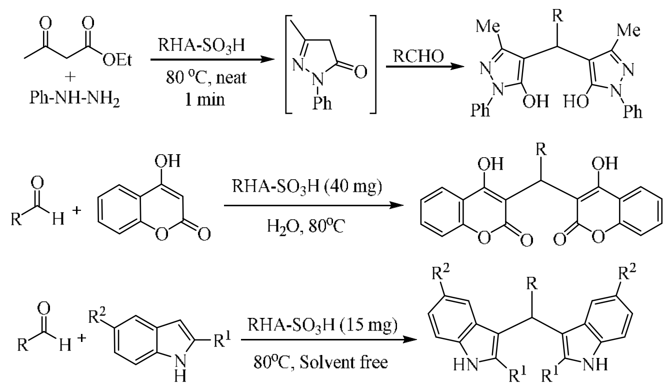
(E) Modification of RHA was done with $FeCl_3$. Characterization of the obtained reagent showed that rice husk ash supported $FeCl_2·2H_2O$ was formed [12]. This reagent was efficiently catalyzed the synthesis of multisubstituted quinolines by the Friedländer heteroannulation of *o*-aminoaryl ketones with ketones or β-diketones under mild reaction conditions. This methodology allows for the synthesis of a broad range of substituted quinolines in high yields and with excellent regioselectivity in the absence of solvent.



(F) Although application of the modified amorphous silica obtained from rice husk ash as the catalyst is useful, the reported method for the preparation of pure silica from rice husk ash needs various stages and a long time [4]. On the basis of these points, Shirini and co-workers showed that it could be used of RHA as catalyst or support for the preparation of the catalysts without need to extraction of pure silica. They used RHA as a green and cheap reagent for the chemoselective protection of various functional groups including *O*-silyl protection of alcohols and phenols, and acetylation of alcohols, phenols, thiols and amines [13]. All reactions were performed under mild conditions in good to high yields.



(G) Sulfonated rice husk ash (RHA-SO_3H) as a highly powerful solid acid catalyst was obtained from the reaction of RHA and chlorosulfonic acid [14]. This reagent is used for the simple and efficient synthesis of some of bis-heterocyclic compounds including 4,4’-(arylmethylene)-bis-(3-methyl-1-phenyl-1H-pyrazol-5-ols), 3,3’-(arylmethylene)-bis-(4-hydroxycoumarins) and bis(indolyl)methanes [15]. High reaction rates, ease of preparation and handling of the catalyst, use of an inexpensive and reusable catalyst are some of advantagesof this method.



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