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Nanostructure sulfated tin oxide as an efficient catalyst for the preparation of 7-hydroxy-4-methyl coumarin by Pechmann condensation reaction

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ABSTRACT

Nanocrystalline sulfated tin oxide with different sulfate contents (5–30 wt%) were prepared from hydroxylated tin oxide obtained by the precipitation method, followed by wet impregnation with SO_4^{2-} species using a sulfuric acid solution. In samples calcined at 400, 500 and 600 °C the characterization of the solids was made by DTA, XRD and nitrogen adsorption. The strength and number of acid sites were determined by nonaqueous titration of n-butylamine in acetonitrile. Both Bronsted and Lewis acid sites were determined by FTIR spectra of pyridine adsorbed. Sulfated tin oxides were tested in the synthesis of 7-hydroxy-4-methyl coumarin via solvent free Pechmann reaction of resorcinol:ethylacetoacetate (molar ratio 1:2), at 120 °C. DTA measurements showed that SO_4^{2-} addition tends to slow down the formation of SnO_2 crystallites. XRD profiles showed that the sulfating inhibits the SnO_2 crystal growth. The SO_4 species remained strongly bonded at the SnO_2 surface stabilizing its crystallite size against sintering and it acts as a structure porogen director mediating nanoparticle growth and assembly yielding a mesostructured form of SnO_2 with wormhole morphology and high thermal stability. The surface areas of the investigated samples were influenced with the sulphate content and calcination temperature. The acidity measurements showed that the total acidity increases with the rise of sulfate content up to 25 wt%. FTIR spectra of pyridine adsorbed on the catalysts showed the presence of both Bronsted and Lewis acid sites.

The formation of 7-hydroxy-4-methyl coumarin increases with the increase of surface acidity showing a maximum when the sulfate content and calcination temperature were 25 wt% and 400 °C, respectively.

1. Introduction

Coumarins occupy an important place in the realm of natural products and synthetic organic chemistry. They have been used as anticoagulants [1], additives in food and cosmetics [2], and in the preparation of insecticides, optical brighteners [3], and dispersed fluorescent and laser dyes [4]. Coumarins have been synthesized by several methods including the von Pechmann reactions [5]. Conventionally, the Pechmann reaction is carried out in presence of concentrated sulfuric acid catalyst [6,7], phosphorous pentaoxide [8], trifluoroacetic acid [9] and aluminum chloride [10]. These acids are corrosive and required in excess amount. Homogeneous metal chlorides such as $ZnCl_4$, $TiCl_4$, $InCl_3$, GaI_3 [11–13], triflates [14], sulfonic acid [15] and ionic liquids [16] are reported to produce 7-hydroxy coumarin derivatives. To avoid such problems, there have been efforts to find environmentally benign alternative and heterogeneously catalyzed synthetic routes. This can be achieved by the development of solid acid catalysts that are stable, regenerable and active at moderate temperatures.

Solid acids have emerged as potential alternate catalysts to homogeneous liquid acids [17,18] due to their non-hazardous nature, requirements in catalytic amounts, enhanced selectivity, the ease of separation without resulting into problem of waste disposal and easier post-reaction work-up. For the synthesis of 7-hydroxy-4-methyl coumarin only few studies are reported [19–22] using solid catalysts. It can be said that solid acids are the most important heterogeneous catalysts used today, considering in terms of both the total amounts used and the final economical impact. SO_4^{2-}/M_xO_y is a new type of solid acid catalyst; it has some advantages such as it has good acid strength, it is quite stable to moisture, air and heat, is easily separated, less corrosive to reactors and containers, and more friendly to the environment [20]. These catalysts are finding numerous applications in oil refinery and petrochemical industries. Many studies have been reported concerning sulfated metal oxides as superacids, where sulfated zirconia (SO_4^{2-}/ZrO_2) and sulfated titania (SO_4^{2-}/TiO_2) which exhibits high catalytic activities for various reactions are typical examples [23–26], it shows strongest super acidity; its acid

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strength is lower than −16 on the Hammett function scale [27]. Commonly, the superacids have been prepared by following the next steps: (i) preparation of amorphous metal oxide gels as precursors; (ii) treatment of the gels with sulfate ion by exposure to a H_2SO_4 solution or by impregnation with $(NH_4)_2SO_4$ and (iii) calcination of the sulfated materials at a high temperature in air. In this way sulfated tin oxide (SO_4^{2-}/SnO_2) is one of the most promising solid acids catalysis with strongest acidity. It has been reported that its acid strength can be comparable to that of SO_4^{2-}/ZrO_2 [28]. Temperature programmed desorption (TPD) of pyridine [29] and temperature-programmed reaction of adsorbed furan [30] indicate the possibility that SO_4^{2-}/SnO_2 has an acid strength higher than that of SO_4^{2-}/ZrO_2. Nevertheless, papers concerning the study of SO_4^{2-}/SnO_2 catalysts have been scarcely reported [31–33] because of the complexity in their preparation, in particular owing to the difficulty to obtain the oxide gels from its salts. Therefore, the study on SO_4^{2-}/SnO_2 superacid is benefiting both on the understanding of the essence of the solid super acid and on the acquaintance of more economic and it can be said that sulfated metal oxides are the most important environmentally friendly heterogeneous catalysts to substitute current liquid acids and halogen-based solid acids, with increasing emphasis on green chemistry [34].

However, to our knowledge the mesoporous SO_4^{2-}/SnO_2 has not yet been explored as a catalyst in Pechmann condensation reaction of 7-hydroxy-4-methyl coumarin. In this work, thermally stable mesostructured tin oxide was synthesized by functionalization of SnO_2 nanoparticles obtained directly by precipitation of chloride precursor with ammonia, without surfactant, and sulfated with sulfuric acid. The SO_4^{2-}/SnO_2 catalysts showed activity during the Pechmann condensation reaction of 7-hydroxy-4-methyl coumarin at 120 °C. Herein also, we aimed to study the effect of sulfate content and calcination temperature on the structural, acidic properties of the examined SO_4^{2-}/SnO_2 catalysts and the synthesis of 7-hydroxy-4-methyl coumarin from resorcinol and ethyl acetoacetate.

2. Experimental

2.1. Catalyst preparation

The oxide gel was prepared by the method described below. In a typical synthesis, 100 g of $SnCl_2{\cdot}2H_2O$ (99% purity) were dissolved in 500 ml of distilled water with vigorous stirring and heating with adding few drops of concentrated HNO_3, then at 30 °C aqueous solution was added dropwise a NH_4OH (25 vol%) solution with continuous vigorous stirring until the solution reach a final pH 8. The pale yellow gel type precipitate obtained was filtered and suspended in a 4% CH_3COONH_4 solution during 30 min. Then, the $Sn(OH)_2{\cdot}xH_2O$ gels were impregnated with the appropriate amount of a 1 M H_2SO_4 solution to obtain 5, 10, 15, 25, and 30 wt% of sulfate. After, the gels were dried at 110 °C for 24 h and calcined at 400, 500 and 600 °C for 3 h. In the designation of these samples, the roman numbers I, II and III refers to the calcination temperatures. The designation 5S-Sn-III indicates the sample containing 5 wt% SO_4^{2-} and calcined at 600 °C.

2.2. Catalyst characterization

2.2.1. Thermal analysis

Thermal analysis (DTA) of the uncalcined samples was carried out using a Shimadzu thermal analyzer, type 50-H. The samples under examination were heated in N_2 stream at a rate of 10 °C/min.

2.2.2. XRD investigation

The powder diffraction patterns were recorded on X-ray powder diffractometer (XRD) PW 150 (Philips) using Ni filtered Cu Kα radiation (λ = 1.540 Å) at 40 kV, 30 mA and a scanning range 2Θ of 18°–60°. The crystallite size (nm) was calculated from the broadening of the strongest peak of SnO_2, peak (1 1 0) at 2Θ = 26.6°, using Debye–Scherrer equation [35]:

$$D = \frac{k\lambda}{\beta \cos \Theta}$$

where k is the crystallite shape constant (≈1), λ is the radiation wavelength (Å), β is the line breadth (radians) and Θ is the Bragg angle.

2.2.3. Surface area measurement

The specific surface areas of the calcined samples were determined from nitrogen adsorption studied conducted at −196 °C using the high vacuum conventional volumetric glass system. Prior to any adsorption measurement the sample was degassed at 250 °C for 4 h under a reduced pressure of 10^{-5} Torr.

2.2.4. Surface acidity measurements

2.2.4.1. Potentiometric titration. The total acidity of the solid samples was measured by means of potentiometric titration [36,37]. The solid (0.05 g) was suspended in 10 ml acetonitrile (Merck), and agitated for 3 h. Then, the suspension was titrated with 0.025 N n-butylamine in acetonitrile at 0.005 ml/min. The electrode potential variation was measured with an Orion 420 digital A model using a double junction electrode.

2.2.4.2. Pyridine adsorption. Lewis and Bronsted acid sites presented on the surface were determined with FT-IR spectra of adsorbed pyridine. Prior to the pyridine adsorption [38], the samples were degassed at 200 °C for 3 h under high vacuum and then the samples were cooled to 30 °C. The dry pyridine was then flashed inside the vacuum system and the samples were maintained under these conditions for one month. Then, the excess pyridine was removed by evaporation. The FT-IR spectra of the samples were conducted using MATTSON 5000 FTIR spectrophotometer; by mixing 0.005 g of the sample with 0.1 g KBr in 30 mm diameter self supporting discs were used.

2.2.5. Catalytic activity

The synthesis of 7-hydroxy-4-methyl coumarin was carried out by using resorcinol (10 mmol) and ethylacetoacetate (20 mmol) with 0.1 g of the activated catalyst (at 120 °C for 2 h). The reaction was carried out in oil bath at 120 °C under stirring and reflux for 2 h. After the reaction, the product was separated by transferring the hot reaction mixture in ice bath and stirring for about 15 min, then filtration. The product was collected by filtration and re-crystallized using ethanol. Finally the product was characterized by GC–MS, ^{1}H NMR analysis and melting point measurement. The % yield of 7-hydroxy-4-methyl coumarin was calculated by different methods [39–41] one of them is as follows [39]:

$$\text{Yield (wt\%)} = \left(\frac{\text{Obtained weight of product}}{\text{Theoretical weight of product}}\right) \times 100.$$

3. Results and discussion

3.1. Thermal analysis (DTA)

The DTA curve of the $Sn(OH)_4$ shows four-steps decomposition behavior: three endothermic and two exothermic decomposition processes (Fig. 1). The first endothermic process occurring from room temperature to 115.1 °C is attributed to a loss of physically adsorbed water. The second endothermic process is abroad one from 180.4 to 380.1 °C, such high temperature dehydration step