



Synthesis and characterization of new solid acid catalysts, H₃PW₁₂O₄₀ supported on nanoparticle tin oxide: An efficient catalyst for the preparation of 7-hydroxy-4-methylcoumarin

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ABSTRACT

A series of 12-tungstophosphoric acid (TPA) modified SnO₂ samples (TPA–SnO₂) with varying TPA content were prepared by wet impregnation technique. The TPA–SnO₂ catalysts were characterized by thermal analysis, powder X-ray diffraction (XRD) patterns and N₂ adsorption at –196 °C. The surface acidity was measured by potentiometric titration and FTIR spectra of chemically adsorbed pyridine. The DTA shows a peak maximum at 600 °C which was ascribed to the crystallization of tin oxyhydroxide into SnO₂. The thermograms of TPA show no exothermic effect due to the decomposition of TPA up to 25 wt%. When TPA content reached 30 wt% TPA/SnO₂ an exothermic effect at 618 °C indicated that the thermal stability of TPA on SnO₂ seems to be comparable to that of pure TPA. XRD measurements showed that there are no diffraction patterns of TPA for the catalyst calcined at 500 °C. The presence of TPA on tin oxide inhibits sintering of the particles during calcination by reducing the crystallite size of SnO₂ from 27.7 to 19.8 nm. The surface area values increase gradually with increasing TPA loading to reach a maximum limit of 25 wt% TPA. When calcination temperature is increased to 500 °C the specific surface is decreased. The acidity measurements showed that the total acidity increases with the rise of TPA content up to 30 wt%. FTIR spectra of pyridine adsorbed on the catalysts showed the presence of both Bronsted and Lewis acid sites. An optimum reaction performance (78.0% of 7-hydroxy-4-methyl coumarin formed) was achieved at 30 wt% loading of TPA calcined at 400 °C and reaction conditions of 120 °C, 2 h reaction and 1:2 (resorcinol:ethyl acetoacetate) molar ratio.

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1. Introduction

Coumarin and its derivatives have been attracting great interest because they occupy a special place in the realm of natural products and synthetic organic chemistry. Among the various coumarin derivatives, 7-substituted coumarin are consisting an important group of coumarin derivatives showing various bioactivities and also other applications [1]. For example, 7-hydroxy-4-methyl coumarin (β -ethylumbelliferone) is used as fluorescent brightener, efficient laser dye, standard for fluorometric determination of enzymatic activity, as a starting material for the preparation of insecticide and furano coumarin [2–4]. Similarly, 7-amino-4-methyl coumarin is mainly used as laser dye and intermediate for the synthesis of bioactive compounds [5]. Pechmann reaction is the most widely used method for preparing coumarin since it starts

from simple starting materials and offers high yield. Mineral acids like H₂SO₄, HCl and H₃PO₄, CF₃COOH and Lewis acids such as ZnCl₂, FeCl₃, SnCl₄, TiCl₄ and AlCl₃ were used as catalysts in the conventional coumarin synthesis [6]. However, most of these acid catalysts are required in stoichiometric amount or more for high yield. They are corrosive, difficult to separate and create severe environmental problems due to disposal of post reaction wastes.

Solid acids have emerged as potential alternate catalysts to homogeneous liquid acids [7,8] 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 [9] using solid catalysts.

Heteropolyacids (HPA) has got extensive studies as an efficient solid acid catalyst due to its unique advantages, such as strong Bronsted acidity, structure alterability and environmental friendliness [10,11]. Nowadays, most studies focus on the catalytic behaviors of the Keggin structured HPA [12], among which

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12-tungstophosphoric acid with the formula of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is known to be a highly active catalyst for a variety of acid-catalyzed reactions [13,14].

Supported heteropolyacids are important for many applications, because bulk HPAs have low specific surface area ($1\text{--}10\text{ m}^2/\text{g}$). In the case of unsupported heteropolyacids, when the reactants have a polar character, the catalytic reactions occur not only at the surface but also in the bulk of the solid heteropolyacids [15]. This is the reason why in spite of their low surface areas, they demonstrate quite high catalytic activity. When non-polar reactants are used, it is important to increase the surface area or even better to increase the number of accessible acid sites of the HPA. This can be achieved by dispersing the heteropolyacids on solid supports with high surface areas [16,17].

Tin dioxide is an n-type wide band-gap with a tetragonal crystalline structure similar to that of rutile [18]. Tin oxide, SnO_2 , has been used in a wide range of applications in sciences, technologies and industries, such as catalysis, conductivity, gas sensing, ceramics, plastics, and antistatic coating [19,20]. It has been synthesized by means of several chemical routes. Nanostructure SnO_2 has been obtained by precipitation [21], sol-gel method [22], polymerized complex [23], amorphous citrate [24] and gel combustion methods [25]. To the best of our knowledge, no report has been made about the use of heterogeneous catalyst of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SnO}_2$ nanoparticle for the synthesis of coumarin via Pechmann condensation reaction.

Herein, the present investigation aimed to study the effect of 12-tungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$, (TPA) content and calcination temperature on the structural, acidic properties of the examined TPA/ 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. About 100 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 500 ml distilled water with vigorous stirring and heating with adding few drops of concentrated HNO_3 . At 30°C NH_4OH solution subjected to bubbling by a current of N_2 gas flowing at a rate of 20 ml/min through the tin chloride solution, the final pH of the solution was adjusted to 8. A buff precipitate was obtained, filtered and washed thoroughly with 2% CH_3COONa solution until all chloride was eliminated (silver nitrate test). The $\text{Sn}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ gel was first dried at 110°C for 24 h, then calcined at 550°C for 4 h.

The SnO_2 were impregnated with the appropriate amount of TPA solution to obtain, 3, 7, 10, 15, 25 and 30 wt% TPA. These samples were dried at 120°C for 24 h, followed by calcination at 400, 500 and 600°C for 4 h. In the designation of these samples, the roman numbers I–III refers to the calcination temperatures. The designation 30TPA–Sn-III indicates the sample containing 30 wt% TPA 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 $10^\circ\text{C}/\text{min}$.

2.2.2. XRD investigations

The powder diffraction patterns were recorded on X-ray powder diffractometer (XRD) PW 150 (Philips) using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.540\text{ \AA}$) at 40 kV, 30 mA and a scanning range 2θ of $18\text{--}60^\circ$. The crystallite size (nm) was calculated from the

broadening of the strongest peak of SnO_2 , peak (1 1 0) at $2\theta = 26.5$, using Scherrer equation.

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

where k is the crystallite shape constant (≈ 1), λ is the radiation wavelength (\AA), 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 by nitrogen adsorption studies 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 [26,27]. 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 FTIR spectra of adsorbed pyridine. Prior to the pyridine adsorption [28], the samples were degassed at 200°C for 3 h under high vacuum followed by soaking suspending in a dried pyridine. Then, the excess pyridine was removed by evaporation. The FTIR 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 products were identified by IR, m.p. and NMR spectral data. The % yield of 7-hydroxy-4-methyl coumarin was calculated as follows:

$$\text{yield (wt\%)} = \frac{\text{obtained weight of product}}{\text{theoretical weight of product}} \times 100$$

3. Results and discussion

3.1. Thermal analysis (DTA)

The DTA analysis of pure TPA hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$), not present here, shows two endothermic effects [29]; the first one occurred at 100°C because of the loss of physisorbed water, the second one is located at 200°C and accounts for the loss of crystallization water. The DTA shows an exothermic peak at 627°C due to the complete decomposition of the Keggin structure to form a mixture of oxides followed by its crystallization.

The tin hydroxide showed two endothermic and two exothermic peaks, Fig. 1. The first endothermic peak from room temperature to 180°C was due to the loss of physisorbed water, and the second peak from 182 to 335°C was ascribed to the dehydration and dehydroxylation of amorphous tin hydroxide. The DTA of the samples shows a broad exothermic peak around 450°C , assigned

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