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## ORIGINAL ARTICLE

# Some physico-chemical properties and catalytic activity of sulfate ion supported on $\text{WO}_3/\text{SnO}_2$ catalyst

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## KEYWORDS

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**Abstract** Solid acid catalyst 15 wt%  $\text{WO}_3/\text{SnO}_2$  was synthesized and loaded with 15 wt%  $\text{SO}_4$ . The obtained catalyst was calcined at 400, 500, 650 and 800 °C. The prepared catalysts were characterized by TG-DTA, XRD, FTIR and  $\text{N}_2$  adsorption at  $-196$  °C. The surface acidity was measured by non aqueous potentiometric titration and FT-IR spectra of chemisorbed pyridine. The catalytic performance was evaluated on the esterification of propionic acid with *n*-butanol in liquid phase. The TG-DTA analysis shows that the decomposition of sulfate species occurred at  $> 500$  °C. XRD measurements showed that  $\text{WO}_3$  dispersed completely on the surface of  $\text{SnO}_2$  and that the sulfating of  $\text{WO}_3/\text{SnO}_2$  tends to hinder the crystallization of  $\text{SnO}_2$ . The specific surface area, total pore volume and micropore volume are increased with increasing thermal treatment up to 500 °C, and then decreased gradually with a further increase in calcination temperature. The prepared catalysts possess very strong acid sites and contain both Brønsted and Lewis acid sites. The total surface acidity decreased with raising of the calcination temperature. The highest conversion of propionic acid was for 400 °C product, and decreased with an increase in calcination temperature. The effect of the reaction parameters, i.e., time of reaction, reaction temperature, and reactant molar ratio and the weight of the catalyst were also studied. The reaction obeys the second order kinetic equation with respect to propionic acid concentration. Brønsted and Lewis acid sites appeared to be needed for catalytic activity in *n*-butyl propionate formation.

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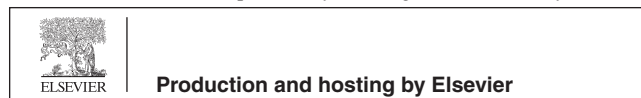
## 1. Introduction

Many reactions in synthetic organic chemistry are acid-catalyzed reactions. These reactions include esterification,

etherification, hydration, hydrolysis, alkylation, isomerization and others. Liquid-phase esterification is an important method for producing various esters. The esters are used in the manufacturing of solvents, plasticizers, plastics, leather, perfumes, medicine...etc. (Ali et al., 2007; Lilja et al., 2002). Conventional mineral acids were used as catalysts in esterification reactions. These homogeneous catalysts suffer from several disadvantages, such as their miscibility with the reaction medium, which causes separation problems, the existence of side reactions, corrosion of the equipment and the need to deal with acidic wastes (Liu and Tan, 2001). The growing awareness of the unacceptability of these liquid catalysts and the resulting legislation give a major

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impetus to the search for cleaner technology. Cleaner technology could be possible by making use of environment friendly heterogeneous catalysts involving the use of solid acids (Sharma et al., 2004).

Metal oxides, mixed oxides, cation exchange resins and zeolites were the most used solid acids (Tanabe, 1981). In the last decade, it is found that the loading of some metal oxides with sulfate ion or acidic high valence metal oxides such as  $\text{WO}_3$  and  $\text{MoO}_3$  causes an increase in the acidity of the catalyst and produces superacids (Yamaguchi, 1990; Arata, 1996). Also, metal oxides and resins may be supported by heteropoly acids or sulfonic acid and show a high activity for esterification reactions (Khder, 2008; Parida and Mallick, 2007; Bahatt and Patel, 2005; Ali et al., 2007; Xi and Cao, 2010). The textural properties, surface acidity and catalytic activity of the catalyst depend on the percentage of loading, calcination temperature and the method of preparation (Khder et al., 2008; Sharma et al., 2004). *n*-butyl propionate ester was synthesized by the catalytic esterification of 1-butanol with propionic acid. The catalysts used for this reaction include sulfuric acid and  $\text{AlCl}_3$  (Rao et al., 1979), ion-exchange resins (Dakshinamurthy et al., 1984; Liu et al., 2006; Lee et al., 2002; Ali et al., 2007; Xi and Cao, 2010), 12-tungstosilicic acid on hydrous zirconia (Bahatt and Patel, 2005) and fibrous polymer-supported sulfonic acid (Lilja et al., 2005).

Many papers concerning the preparation, characterization and catalytic activity of  $\text{WO}_3$ - $\text{SnO}_2$  catalysts were reported (Ai, 1984; Arata and Hino, 1993; Maksimov et al., 2000; Arata et al., 2000; Ma et al., 2000; Hino et al., 2006, 2007; Pimtong-Ngam et al., 2007; Khder and Ahmed, 2009; Shouli et al., 2010; Sarkar et al., 2010). But, no papers concerning sulfated  $\text{WO}_3/\text{SnO}_2$  catalysts were found.

In the present investigation, we have prepared a 15 wt%  $\text{WO}_3/\text{SnO}_2$  support loading it with 15 wt%  $\text{SO}_4$ . The effect of calcination temperature on the structural and textural properties, as well as on the surface acidity was investigated. The catalytic activities of the obtained catalysts were tested by esterification of propionic acid (PA) with *n*-butanol (B). Further, the effect of various reaction parameters on the catalytic activity was also studied.

## 2. Experimental

### 2.1. Materials

Pure tin oxide gel was prepared by a dropwise addition of ammonia solution (10 wt%) to 0.5 M solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (Riedel-deHaen) with vigorous stirring for 4 h, the final pH of the gel was adjusted to 8. The gel was left overnight washed by decantation with 1 wt% ammonium acetate solution (Matsushashi et al., 1990) until all chloride ions were eliminated (silver nitrate test), then washed with double distilled water and finally dried at 120 °C. Appropriate amount of ammonium paratungstate (APT) solution (30 g/L) (Prolabo) was added to the dry tin hydroxide gel, to obtain 15 wt%  $\text{WO}_3$  loading, with vigorous stirring for 4 h. The product was left overnight then dried at 120 °C. The  $\text{WO}_3/\text{SnO}_2$  support was sulfated by the addition of an appropriate amount of 1 M  $\text{H}_2\text{SO}_4$  solution, to obtain 15 wt%  $\text{SO}_4$  loading, with stirring for 4 h, followed by drying at 120 °C for 24 h. The prepared catalyst was calcined in air at 400, 500, 650 and 800 °C for 4 h. The samples were designated as SWS-*x*, where *x* represents the calcination temperature.

### 2.2. Techniques

Thermal analysis (TG-DTA) of uncalcined sample was carried in air atmosphere using Linseis Thermal Analyzer, Type STA PT-1600 (Germany). A weight of ~45 mg was placed in a crucible of 100  $\mu\text{L}$  capacity. The run was followed between 25 and 800 °C at a heating rate of 10°/min.

The X-ray powder diffractograms, of the samples calcined at 500 and 800 °C were recorded on Philips Diffractometer Type PW (1830). The pattern was obtained with Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 30 mA, with a scanning speed of 1° in  $2\theta$ , and a scanning range  $2\theta$  of 20–70°. The spacing *d* corresponding to  $2\theta$  of the peaks was calculated and correlated with that of ASTM to determine the phases existing.

The FT-IR spectra of the samples were recorded using Jasco FT-IR-460 spectrophotometer in the range of 1200–1700  $\text{cm}^{-1}$ , at a resolution of 4  $\text{cm}^{-1}$ ; by mixing 0.005 g of the sample with 0.1 g KBr in 30 mm diameter self supporting disks were used.

The textural properties of all the samples were determined from the analysis of the data of nitrogen adsorption at 77 K, using Gemini III 2375 Surface Area Analyzer apparatus. Prior to any adsorption measurement, the sample was degassed at 200 °C for 6 h under a reduced pressure of  $10^{-4}$  Torr.

The total acidity of the solid samples was measured by means of potentiometric titration method (Rao et al., 2006; Bennaradi et al., 2007). The dry solid (0.1 g) was suspended in 10 mL acetonitrile (Lab-Scan), and agitated for 3 h. Then, the suspension was titrated with 0.1 N *n*-butylamine (Merck) at 0.05 mL/min. The electrode potential variation was measured with Inolab Digital pH-mV model using a double junction electrode. The nature of acid sites presented on the surface of the catalyst was determined with FTIR transmission spectra of adsorbed pyridine (Scharlau) at the range of 1200–1700  $\text{cm}^{-1}$ . Prior to the pyridine adsorption (Khder et al., 2008; Khder and Ahmed, 2009), the samples were degassed at 200 °C for 3 h under high vacuum followed by suspending in a dried pyridine. Then, the excess pyridine was removed by evaporation at 70 °C.

The catalytic activity of the prepared catalysts was tested for the esterification of propionic acid (Merck) with *n*-butanol (SRL). The esterification reaction was carried out in a 100 mL flat-bottomed flask, equipped with a reflux condenser, containing a stirring mixture of propionic acid (0.05 M), *n*-butanol (0.10 M) and the catalyst (0.2 g). The stirring rate in all the experiments was 600 rpm. The reaction mixture was stirred at 110 °C for 4 h. After that, the reaction mixture was immediately filtered and quenched to stop the reaction. Liquid samples (0.5 mL) were withdrawn and the amount of unreacted acid was analyzed by titration with 0.1 N NaOH. The effects of reaction temperature, weight of the catalyst, the initial molar ratio between the acid and alcohol, calcination temperature and the time of reaction were studied.

## 3. Results and discussion

### 3.1. Thermal analysis

Fig. 1 shows the TG-DTA curves of the dried catalyst. The TG curve shows four characteristic steps at 50–200, 200–480, 480–560 and 560–770 °C with a weight loss of 4.2, 2.0, 7.0 and

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