Applied Catalysis A, General 560 (2018) 119–131

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Efficient solid acid catalysts based on sulfated tin oxides for liquid phase esterification of levulinic acid with ethanol

Margarita Popova[a,*], Pavletta Shestakova[a,*], Hristina Lazarova[a], Momtchil Dimitrov[a], Daniela Kovacheva[b], Agnes Szegedi[c], Gregor Mali[d], Venkata Dasireddy[d], Blaž Likozar[d], Nicole Wilde[e], Roger Gläser[e]

[a] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113, Sofia, Bulgaria
[b] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113, Sofia, Bulgaria
[c] Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, Hungarian Academy of Sciences, 1117, Budapest, Hungary
[d] National Institute of Chemistry, Hajdrihova 19, 1001, Ljubljana, Slovenia
[e] Universität Leipzig, Institute of Chemical Technology, 04103, Leipzig, Germany

ARTICLE INFO

Keywords:
Nanosized tin oxide
Sulfated catalysts
Ethyl levulinate
Esterification
Biomass
Solid state NMR

ABSTRACT

Tin oxide nanomaterials prepared by hydrothermal synthesis at 100 °C or 140 °C with or without template and further calcination step were modified with sulfate groups by post synthesis treatment. The catalysts were characterized by X-ray powder diffraction (XRD), N_2 physisorption, UV Vis spectroscopy, TG analysis, XPS and solid state NMR spectroscopy. The acidity of the materials was characterized by temperature programmed desorption (TPD) of ammonia. The catalytic performance of nanosized SnO_2 catalysts and their sulfated analogues was studied in levulinic acid (LA) esterification with ethanol. Sulfated materials show significantly higher activity compared to non-sulfated ones. It was found that the synthesis parameters (temperature, template) for preparation of the parent SnO_2 nanoparticles influence significantly their textural properties and have a pronounced effect on the structural characteristics of the obtained sulfated tin oxide based materials and their catalytic performance in levulinic acid esterification. Skipping the calcination step during the preparation of parent SnO_2 samples synthesized without template resulted in the formation of new, highly crystalline phase based on hydrated tin(IV) sulfate [$Sn(SO_4)_2.xH_2O$], tin(IV) bisulfate [$Sn(HSO_4)_4.xH_2O$] and/or tin(IV) pyrosulfate [$Sn(S_2O_7).xH_2O$] species in the sulfated nanomaterials with superior catalytic performance. The formation of this new and catalytically very active phase not reported so far in the literature for sulfated tin oxide-based materials is discussed. The catalytically active sites for esterification of levulinic acid with ethanol is suggested to result from the formation of strong Brønsted and Lewis acid sites with high density in the newly registered phase. The results indicate that the chemical structure and catalytic performance of the obtained sulfated tin oxide based materials strongly depend on the treatment of the SnO_2 nanoparticles before the sulfation procedure.

1. Introduction

In the recent years, lignocellulosic biomass has been intensively studied for production of chemicals, fuels and energy. Levulinic acid and its esters are promising platform chemicals for the production of a broad range of sources for the biofuel, polymer and fine chemicals industry [1–5]. Levulinic acid (LA) is generally produced by the acid-catalyzed hydrolysis of cellulose, and can be converted into levulinate esters, γ-valerolactone, 1,4-pentanediol and 5-nonanone (via pentanoic acid) as well as diphenolic acid as an intermediate for the synthesis of epoxy resins and poly-carbonates [6–20]. Levulinate esters are also valuble compounds that can be used as fuel additives, solvents and plasticizers. In particular, ethyl levulinate can directly be used up to 5 wt. % as a diesel-miscible biofuel in regular diesel car engines without modification because of its physicochemical properties similar to those of fatty acid methyl esters (FAME), i.e., biodiesel [6]. Therefore ethyl levulinate has the potential to decrease the consumption of petroleum-derived fossil fuels. Generally, levulinate esters are produced by esterification reactions using mineral acids such as HCl, H_2SO_4 and H_3PO_4, resulting in the high yield of the corresponding products within a short reaction time. However, in such homogeneously catalyzed reactions, the acid catalysts are unrecyclable and often lead to technological

---

[*] Corresponding authors.
E-mail addresses: mpopova@orgchm.bas.bg (M. Popova), psd@orgchm.bas.bg (P. Shestakova).

https://doi.org/10.1016/j.apcata.2018.04.041
Received 7 January 2018; Received in revised form 18 April 2018; Accepted 28 April 2018

problems, e.g., use of a large volume of base for neutralization and corrosion of equipment. The replacement of homogeneously catalyzed reactions with heterogeneously catalyzed analogues in which the catalysts are easily separable and reusable is thus highly desirable [20–30]. In comparison to zeolites, over sulfated metal oxide, e.g., SO_4^{2-}/Nb_2O_5, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, as catalysts higher conversions (up to 44% conversion on SO_4^{2-}/SnO_2 at 70 °C) in the levulinic acid esterification is registered due to the presence of stronger acid sites. The acid site strength of SO_4^{2-}/SnO_2 is reported to be higher than that of SO_4^{2-}/ZrO_2 [2]. The increase in the surface acidity strength of the modified oxides leads to the raise in activity of the catalyst. The acidity generated by modification of SnO_2 with sulfate anions is even stronger than pure sulfuric acid. Thus it can be consider as super acid catalysts for many commercially important reactions, such as hydrocracking of paraffins, dehydration of alcohols, esterification, alkylation of olefins and protection of aldehydes, ketones and alcohols and olefins [31]. However, a detailed explanation on the nature of the active acid sites (Brønsted and Lewis) and the mechanism of their formation is still missing.

Different procedures are suggested in the literature for the preparation of sulfated tin oxide with strong acid sites. H. Miyazaki et al. [32] reported the preparation of a highly active sulfated tin oxide from tin oxide gel, precipitated by the hydrolysis of $SnCl_4$. A. A. Dabbawala et al. [33] revealed the role of different sulfur content (1–8 wt%) during thermal decomposition of stannous sulfate during the preparation of sulfated tin oxides]. The sulfation procedure was carried out by impregnation of tin(IV) hydroxide with 0.5 M sulfuric acid resulting in the preservation of tin(IV) oxide tetragonal phase, decrease of the crystallite size and increase in the specific surface area. The effect of sulfate content and calcination temperature on the structure, acidity and catalytic activity of tin oxide was studied by A.S. Khder et al. [34] as well. They found that the sulfation enhances the concentration of Brønsted acid sitesand increases the strength of Lewis acidity when 20 wt.% SO_4^{2-} groups are applied and calcination is carried out at 550 °C.

In the already published papers the SnO_2 phase detected in sulphated materials showed similar crystalline properties to the parent SnO_2 materials thus suggesting that the sulfation procedures affected only surface of SnO_2 nanoparticles while their bulk structure remained unchanged. The increased catalytic activity of the sulfated tin oxides is considered to be a result of the formation of SO_4^{2-}/SnO_2 chelate structures of different coordination modes between SO_4^{2-} and SnO_2 which is associated with an increased concentration of Brønsted and Lewis acid sites. However the problem related to the low stability in liquid phase reactions and the considerable leaching of the active phase of surface SO_4^{2-}/SnO_2 species during the catalytic experiments which is more pronounced in comparison to SO_4^{2-}/ZrO_2 remains a major challenge [2,35,36]. Despite the strong acidity of the sulfated metal oxides their application is limited due to the leaching of sulfate groups during the reaction which is the most important drawback of this type of catalysts [33,34]. Moreover, to the best of our knowledge the exact chemical and structural nature of the active sites in sulfated tin oxide nanoparticles are still not fully clarified in the literature.

In the present study, a series of sulfated tin oxide based catalysts and their catalytic activity in the esterification of levulinic acid with ethanol were studied. We used different approaches to prepare active sulfated species in tin oxide based nanomaterials and to stabilize them on the support during the catalytic reaction. The parent SnO_2 materials were synthesized by hydrothermal treatment with or without further calcination step and in the presence or absence of a template. The influence of the textural and morphological properties of the parent SnO_2 prepared under different synthesis conditions on the properties of the sulfated SnO_2 based catalysts was investigated.

2. Experimental part

2.1. Synthesis of nanosized SnO_2 materials

Nanosized SnO_2 samples were synthesized by precipitation of $SnCl_4$ solution with 20% NH_4OH in the presence or absence of template followed by hydrothermal treatment. In a typical preparation, N-hexadecyl-N,N,N-trimethylammoniumbromide (12.0 g) was dissolved in 100 ml distilled water. To this solution was added slowly and under vigorous stirring a second solution of $SnCl_4$ (7.60 g) in 50 ml distilled water. Then the temperature was raised to 50 °C and stirred for 30 min before adding dropwise 40 ml NH_3 (12.5%). The resulting mixture was stirred overnight at 50 °C. Then it was transferred into an autoclave and treated at 100 °C or 140 °C for 24 h. The hydrothermal treatment was followed by filtration of the solution and washing with distilled water, then drying at room temperature was applied. Some of the samples were calcined up to 500 °C with a ramp of 1° per minute and a swelling time of 15 h at the final temperature. In the case of template-free samples the $SnCl_4$ (7.60 g) was added to 100 ml distilled water instead of 50 ml.

2.2. Functionalization of nanosized SnO_2 by SO_4^{2-} groups

Nanosized SnO_2 samples were mixed with 10% wt. H_2SO_4 solution (40 ml/1 g SnO_2). The suspension was dried at ambient temperature and calcined at 300 °C for 3 h. The samples after sulfation are denoted as $SO_4^{2-}/SnO_2(x)(y)$ or $SO_4^{2-}/SnO_2(x)T(y)$, where **x** is temperature of hydrothermal synthesis; **y** is the calcination temperature and **T** indicates the use of template during the synthesis.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected within the range of 10–80° 2θ with a constant step of 0.02° 2θ and counting time of 1 s/step on Bruker D8 Advance diffractometer equipped with Cu Kα radiation and LynxEye detector. Mean crystallite sizes were determined by the Topas-4.2 software package using the Laue formula for the integral breadth (IB) of the diffraction peaks and fundamental parameters peak shape description for the instrumental broadening and diffractometer geometry.

Nitrogen physisorption measurements were carried out at −196 °C using Tristar 3000 Micromeritics volumetric adsorption analyzer. Before the analysis, the samples were outgassed under high vacuum for 2 h at 250 °C. The pore-size distributions were calculated from the desorption isotherms by the BJH method.

Ammonia temperature-programmed desorption (NH_3-TPD) was carried out using a Micromeritics 2920 Autochem II Chemisorption Analyser. The catalyst was pre-treated at 500 °C (at 300 °C for $SO_4^{2-}/SnO_2(100)$ and $SO_4^{2-}/SnO_2(140)$) under the stream of helium for 60 min. Then the temperature was decreased to 80 °C. A mixture of 9.8% NH_3 in He was passed over the catalyst at a flow rate of 25 mL/min for 60 min. The excess NH_3 was removed by purging with helium for 25 min. The temperature was then raised gradually to 900 °C by ramping at 10 °C/min under the flow of helium and desorption data were recorded. The TCD signals were calibrated using various gas concentrations of NH_3 ranging from 0 to 10 wt. % NH_3 in He. The desorbed amount of NH_3 was determined continuously in a thermal conductivity cell and by absorption in a trap containing 0.05 M H_2S0_4 followed by titration with 0.05 M NaOH solution.

The surface chemical composition of selected samples was analyzed by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on AXIS Supra electron spectrometer (Kratos Analitycal Ltd.) using monochromatic Al Ka radiation with photon energy of 1486.6 eV. The energy calibration was performed by normalizing the C1s line of adsorbed adventitious hydrocarbons to 284.6 eV. The binding energies (BE) were determined with an accuracy of ± 0.1 eV.