Journal of Alloys and Compounds 575 (2013) 285-291

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Surface acidity and catalytic activity of aged SO_4^{2-}/SnO_2 catalyst supported with WO₃

M. Nasouh Alaya*, Marwa A. Rabah

Department of Chemistry, Faculty of Sciences, Aleppo University, Syria

ARTICLE INFO

Article history: Received 23 January 2013 Received in revised form 17 May 2013 Accepted 21 May 2013 Available online 4 June 2013

Keywords: WO₃/SO²⁻₄/SnO₂ Surface acidity Adsorbed pyridine Esterification

ABSTRACT

New solid acid was prepared by loading of aged 15 wt.% SO_4^2 / SnO₂ catalyst with 15 and 35 wt.% WO₃. The catalysts were calcined at 400 and 650 °C. The surface areas of the catalysts were determined by the data of N₂ adsorption at -196 °C. The surface acidity was measured potentiometricaly using *n*-butylamine solution in acetonitrile. The types of acidic sites were determined by FT-IR spectra of adsorbed pyridine. The catalytic activities of the catalysts were tested toward esterification of propionic acid (PA) with *n*-butanol (B). The *S*_{BET} values of the ISS were decreased with an increase in the calcination temperature, whereas, the *S*_{BET} of the loaded catalysts was maximum at 400 °C. The results reveal that the used catalysts possess very strong acid sites and contain both Brønsted and Lewis acidic sites. The acid strength, total surface acidity and the conversion of PA were maxima for 400 °C products. The effect of the reaction parameters was also studied, and shows that the PA conversion was increased with an increase in the reaction temperature and the catalyst weight. The reactant molar ratio shows a maximum conversion at PA:B = 1:2. The kinetics study indicates that the catalytic esterification of PA with B obey first order kinetics equation.

The results were compared with previously prepared non-aged catalysts. The comparison reveals that the aging of the support would causes a decrease in S_{BET} , acid strength and catalytic activity, but increases the acid amount of the catalyst.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Solid acids and superacids have prominent advantage over regular mineral acids or Lewis acids as much as that they do not require large quantities of noxious, corrosive reagents, and to avoid difficulties that emerge from handling, post reaction separation, recovery, recycling, and contamination [1,2]. Lately, numerous research outputs have been compensated in developing different superacids as green chemicals to implement environmental regulations [3-5] and to substitute the use of hazardous conventional acid catalysts [6]. Mechanism involves the utilization of superacids is to provide an environment to create and maintain cations supplier, which are useful as intermediate molecules in numerous reactions such as those used for theoretical research [7] and synthetic applications of isomerization [8,9], cracking [10], dehydration [10,11], alkylation [12], acylation [13], Friedel-Crafts reaction [14,15], removal of volatile organic compounds (VOC) [16], hydration [17], esterification [2,18–24] and Pechmann condensation reactions [25].

Among various solid acid catalysts some metallic oxides (e.g. alumina, titania, zirconia and SnO₂), mixed metal oxides, ion ex-

* Corresponding author. Tel.: +963 944359267.

E-mail address: mnalaya@myway.com (M.N. Alaya).

change resins and zeolites [26,27], the load of some metal oxides with sulfate, WO₃ or MoO₃ have emerged as powerful catalysts due to their super-acidity, high activity, and selectivity [3,5,28]. Tin oxide is an *n*-type semiconductor with a large band gap $(E_a = 3.6 \text{ eV})$, also it is stable and sensitive to gases. These properties make the uses of this oxide as a promising material for gas senfilms, photo-catalyst, sors. transistors, photocells, thin optoelectronic devises and negative electrodes for lithium batteries and as catalyst [29-35]. Concerning the catalytic uses it is reported that SnO₂ is an active catalyst for many reactions due to its stability, acidic, basic, oxidizing and reducing surface properties [36]. Recently, it has been proved that the acid strength and catalytic activity of sulfated tin oxide are higher than that of other sulfated metal oxides [5,10,28,37]. On the other hand, it is found that when some oxides are supported with WO₃ and calcined at high temperatures (800–1200 °C), exhibit acidity and catalytic activity for some reactions as skeletal, cracking of isopentane [38], esterification of *n*-octanic acid with methanol [8], dehydration of alcohols and cracking of cumene [10], and biodiesel production [39]. It is also found that loading of MCM-41 with polytungstophosphoric acid (PWS) produces solid acid catalysts used for Pechmann reaction, esterification and Friedel-Craft reactions [40].

Generally, superacid sites of sulfated and tungstated metal oxides are not created by impregnation on the crystallized oxides, but







^{0925-8388/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2013.05.145

on the amorphous forms of metal oxides. The loading of oxides with sulfate and tungstate ions causes an increase in the surface area and surface acidity due to the retardation of oxides crystal forming [5]. Their textural properties, surface acidity and catalytic activity are dependent largely on the percentage of loading, preparation methods and thermal treatment [3,7,14,17,37,41–45].

Concerning esterification reaction, it is one of the fundamental acid-catalyzed reactions. The esters are good solvents and play a major role in the production of flavors, fragrances, plasticizers, plastics, medicinal and surface-active agents [20]. *n*-butyl propionate ester (*n*-BPE) possesses a high boiling point temperature (146.7 °C), a high electrical resistance and a good non-VOC solvent. Many research offers have been given to prepare *n*-BPE by using solid acid catalysts utilizing cation exchange resins [18–20], PWP supported on alumina [2], 12-tungstosilicic acid supported on zirconia [21], and fibrous polymer-supported sulphonic acid [22]. Nevertheless, papers concerning the esterification of propionic acid with *n*-butanol over sulfated SnO₂ or WO₃/SO₄^{2–}/SnO₂ catalysts are rare [23,24].

We have previously prepared and characterized a series of catalysts based on non-aged 15 wt.% SO_4^{2-}/SnO_2 support loaded with 5–45 wt.% WO₃ and exploited to optimize a model catalytic system for esterification of propionic acid with *n*-butanol [23]. In the present investigation, however, we have prepared aged 15 wt.% $SO_4^{2-}/$ SnO_2 hydrogel support, dried, then loaded with 15 and 35 wt.%WO₃. The prepared catalysts are calcined at 400 and 650 °C. The effect of WO₃ loading and calcination temperature on the surface area, surface acidity and catalytic activity toward propionic acid esterification with *n*-butanol are studied.

2. Experimental

2.1. Catalysts

Pure tin oxide hydrogel is prepared by a dropwise addition of ammonia solution (10 wt.%) to 0.5 M solution of SnCl₄·5H₂O (Riedel-deHaen) up to the final pH of 8 with continuous stirring for further 4 h. The gel is left overnight then washed by decantation in sequence with solution of 1% ammonium acetate (Merck) [46,47], followed by bidistilled water. Appropriate amount of 1 M H₂SO₄ solution is added with vigorous stirring for 4 h to the hydrogel making the final sulfate ion percentage up to 15 wt.%. The obtained gel is aged for 24 h at room temperature, then filtered and finally dried at 120 °C. The resulting product is designated hereafter as ISS.

Appropriate amounts of ammonium paratungstate (Prolabo) solution are added to known amounts of ISS catalyst, with stirring for 4 h, to make the percentage loading up to 15 and 35 wt.% WO_3 , and then dried at 120 °C. The obtained materials are calcined in air at 400 and 650 °C for 4 h. The catalysts are designated hereafter as 15 IWSS and 35 IWSS, respectively, followed by a number indicating the calcination temperature.

2.2. Techniques

The specific surface area (S_{BET}) is determined by the analysis of data of nitrogen adsorption at -196 °C, using Gemini III 2375 Surface Area Analyzer. Prior to any adsorption measurement, the sample is degassed at 200 °C for 6 h under a reduced pressure of 10^{-4} Torr.

The surface acidity (strength and amount) of the prepared catalysts is measured by means of potentiometric titration method [48,49]. That is performed by suspended 0.2 g of the dry solid in 20 mL acetonitrile (Lab-Scan), and agitated for 3 h. Then, the suspension is titrated with 0.02 N or 0.1 N *n*-butylamine (Merck) in acetonitrile at 0.05 mL/min. The electrode potential variation is measured with Inolab Digital pH-mV model using a double junction electrode. The initial electrode potential (E_i , mV) measures the strongest acid strength. The nature of acid sites presented on the surface of the catalyst is determined from FT-IR transmission spectra of adsorbed pyridine (Scharlau) within the range of 1200–1700 cm⁻¹ (at a resolution of 4 cm⁻¹) using Jasco FTIR-460 spectrophotometer. Prior to the pyridine adsorption [37,49], the samples are degassed at 200 °C for 3 h under high vacuum followed by suspending in a dried pyridine. The excess pyridine is removed by evaporation at 70 °C. A mixture of 0.005 g sample with 0.1 g of KBr is pressed into 13 mm disks.

The catalytic activity of the prepared catalysts is tested for the esterification of propionic acid (Merck) with *n*-butanol (SRL). The esterification reaction is carried out in 100 mL flat-bottomed flask, equipped with a reflux condenser, containing a stirring mixture of propionic acid (0.05 mol), *n*-butanol (0.10 mol) and 0.2 g of

the prepared catalyst. The reaction mixture is kept at 110 °C with stirring speed of 600 rpm for 4 h, the reaction mixture then immediately filtered and quenched to stop the reaction. Liquid samples of 0.5 mL volume are withdrawn and the amount of unreacted acid is determined by the titration with 0.1 N NaOH. The effects of reaction time, reaction temperature, weight of the catalyst, the initial molar ratio between the acid and alcohol (PA:B), and calcination temperature are all studied.

3. Results and discussion

3.1. Specific surface area

The specific surface areas (S_{BET}) of the catalysts are determined from the nitrogen adsorption at -196 °C. The S_{BET} values are presented in Table 1 and reveal the following points: (i) The addition of sulfate ions to the SnO₂ hydrogel causes a pronounced increase in the surface area. The main reason for the increase in surface area is the retardation of crystallization by sulfate treatment. (ii) The S_{BET} of ISS catalyst is decreased with the increase in the calcination temperature. (iii) The loading of ISS catalyst with WO₃ causes a gradual decrease in S_{BET} for the 200 and 400 °C products, whereas, the S_{BET} is increased gradually with WO₃ loading for 650 °C products. The maximum S_{BET} is observed at 400 °C for WO₃-loaded catalysts. (iv) The surface areas at 650 °C are higher than that of pure SnO₂ which means that the addition of both sulfate ions and WO₃ hinder the crystallization and sintering of SnO₂.

3.2. Surface acidity measurements

The surface acidity measurements of the prepared catalysts by means of potentiometric titration with *n*-butylamine in acetonitrile [48-50] are used to estimate the amount of acid sites and their relative acid strengths according to the value of the initial electrode potential (E_i) . *n*-butylamine is a strong base and can be adsorbed on acid sites of different strengths and types, thus it titrates both Lewis and Brønsted sites [26]. On the other hand, the acid strength of these sites can be classified according to the following scale [2]: $E_i > 100 \text{ mV}$ (very strong sites), $0 < E_i < 100 \text{ mV}$ (strong sites), $-100 \le E_i \le 0$ mV (weak sites) and $E_i \le -100$ mV (very weak sites). Fig. 1 shows the titration curves obtained from the calcined catalysts. The computed amount of the acid sites (mmol/g) and the number of the acid sites per m² (N/m²) as well as the values of E_i are listed in Table 1. For comparison, the surface acidities of SnO₂-400 and SnO₂-650 catalysts are presented in the table.

The results of the acidity measurements reveal the following points: (i) The investigated catalysts possess very strong acid sites, with *E*_i values that are in the range of 135–396 mV. (ii) Mixing of SnO₂ hydrogel with 15 wt.% sulfate ions enhances the acid strength as well as the amount of surface acidity of the catalyst due to the formation of new strong acid sites. (iii) Calcination of the catalysts at 400 °C causes a pronounced increase in the surface acidity, whereas, the raising of the calcination temperature to 650 °C is accompanied with a sharp decrease in the strength and amount of acid sites which may be due to the loss of surface OH groups as well as the decomposition of sulfate ions. (iv) Loading of ISS catalyst with WO₃ causes a slight decrease in the surface acidity for 400 °C products, whereas, no change in the surface acidity is observed for 650 °C products. The number of acid sites per m² (DSA) is decreased slightly due to the gradual increases of the surface area with an increase in the WO₃ loading. (v) The increase of WO₃ loading causes a slight increase in the acid strength, total amount and the number of acid sites for 400 °C products.

The Brønsted and Lewis acidic sites of the catalyst can be characterized using pyridine as a probe molecule. The distribution of both types of acidic sites on the catalysts is confirmed by FT-IR techniques. The FT-IR spectra of the chemisorbed pyridine on the

Table 1	
Surface acidity of $IWO_3/SO_4^{2-}/SnO_2$ catalysts determined from potentiometric titration by <i>n</i> -butylamine in acetonitrile.	

Catalyst	$S_{\text{BET}}(m^2/g)$	E_i (mV)	Acid amount (mmol/g)	$DSA (N/m^2) 10^{-17}$
SnO ₂ -400	55.5	113	0.016	1.715
SnO ₂ -650	14.6	112	0.180	7.416
ISS-200	140.8	135	0.163	6.973
ISS-400	112.6	396	0.515	27.65
ISS-650	28.23	170	0.096	20.48
15 IWSS-200	96.54	218	0.140	8.734
15 IWSS-400	105.3	322	0.280	16.02
15 IWSS-650	31.18	175	0.078	15.07
35 IWSS-200	81.31	200	0.094	6.963
35 IWSS-400	83.71	348	0.290	20.87
35 IWSS-650	39.69	177	0.097	14.72



Fig. 1. Represents the potentiometric titration curves using *n*-butylamine in acetonitrile.

surface of the catalysts calcined at 400 and 650 °C are shown in Fig. 2. The spectra show bands at 1340–1440 cm⁻¹ indicating the adsorption of pyridine by hydrogen bonds [26,51]. The bands appeared at 1540, 1636 and 1649 cm⁻¹ are attributed to the adsorbed pyridine on Brønsted acidic sites with the formation of pyridinum ions [26,48,50,51]. The bands appeared at 1456, 1507, 1558, 1575 and 1618 cm⁻¹ are assigned to the adsorbed pyridine on Lewis acidic sites [26,48,52,53]. In addition, all the spectra exhibited bands at 1490 cm⁻¹ which are attributed to the adsorption of pyridine on Brønsted or/and Lewis acidic sites [41,50,52] or the presence of the adjacent Brønsted and Lewis acidic sites [40]. The

spectra also show that the intensities of the bands for the modified catalysts are decreased with the increasing of wt.% WO_3 loading as well as the raising of the calcination temperature.

The generation of strong Lewis acidic sites by sulfate species may be attributed to the presence of surface sulfur complex which has a covalent S=O bond, which acts as electron-withdrawing species that stimulates the inductive effect (structure A, Scheme 1). Thus, the inductive effect of S=O makes the Lewis acid strength of Sn⁴⁺ very strong [54]. On the other hand, the presence of water or OH-surface groups on the surface of the catalyst give Brønsted acid sites, and the adsorption of water molecule may convert Lewis



Fig. 2. Represents the FT-IR of adsorbed pyridine on prepared catalysts.



Scheme 1. Suggested structures binding of; (A) sulfate groups on the surface of SnO₂, and (B) WO₃ directly with SnO₂ surface and/or with sulfate groups on the surface of SnO₂.

acidic sites to Brønsted acidic sites. Loading of WO₃ on the surface of ISS followed by calcination causes changes in the textural and acidic properties and leads to tungsten-support interactions. These interactions may occur by different manners, e.g., WO₃ is likely to replace sulfate groups and interact directly with SnO₂ surface and/ or interact with sulfate groups on the surface of SnO₂ as shown in structures B, Scheme 1 [51]. It is clear from Table 1 that the addition of WO₃ is accompanied by a decrease in the surface acidity and the surface area, which may be due to the presence of WO₆ groups on the surface. Moreover, samples with higher WO₃ content or higher calcination temperature (650 °C) exhibit an increase in the surface acidity and S_{BET} that are probably due to the agglomeration of crystalline WO₃ on the surface and the decomposition of sulfate ions.

3.3. Catalytic activity

The esterification of carboxylic acids with various alcohols is an electrophilic substitution reaction. The reactions are extremely slow which may be enhanced by thermal activation or by an acid catalyst of either, Brønsted acid [2,22] or Lewis acid [37]. Generally, the esterification reaction is dependent on several parameters, such as, the reaction time, reaction temperature, catalyst amount, reactant molar ratio, and stirring speed [37]. The effects of some parameters on the esterification of propionic acid with *n*-butanol over the prepared catalysts are investigated hereafter. It is found elsewhere that the acid conversion in the esterification of propionic acid with 1-propanol or other alcohols is independent on stirring speed of 200 rpm and above [20]. Therefore, a stirring speed of 600 rpm is maintained during all the experiments.

3.3.1. Effect of reaction time

The effect of the reaction time on PA conversion is studied over the catalysts calcined at 400 °C using 0.20 g catalyst and with reactant molar ratio of PA:B = 1:2 at 110 °C. The results are represented in Fig. 3, and indicate that the percentage conversion of PA has sharply increased with time up to 3 h with yields of 75.98%, 70.97% and 65.46% attained over SS, 15 IWSS and 35 IWSS, respectively. The conversions have slightly increased after 4 h to yield 78.52%, 76.98% and 71.97%, and reach at the end of 6 h the values of 81.48%, 80.98% and 73.97% respectively. The selectivity in using these catalysts towards *n*-butyl propionate remains the same, i.e. 100%. The time of 4 h is taken hereafter to optimize the reaction parameters.

Kinetic data reported on esterification of propionic acid with *n*butanol are relatively scarce in the open literature. Study of this reaction over cation exchange resins [1] and SWS catalysts [24] indicate that the reaction obeys a second order equation with respect to propionic acid concentration. However, esterification of acetic acid with alcohols over zeolites [55] or over SO_4^{2-}/SnO_2 [37] has found to obey a first order reaction. In this work, however, the kinetic data of the esterification of PA with B over the prepared catalysts calcined at 400 °C are shown in Figs. 3 and 4. The plots of -ln (1-conv.) or 1/[PA] with time are linear over a considerable range of time, (up to 2 h). The slope of the linear part is a measure of the specific reaction rate constant. Table 2 shows the values of the reaction rate constants by applying the first order and second order equations. It is obvious from data and R^2 values that the reaction follows first order kinetics with respect to acid rather than the second order kinetics.

The values of the rate constants reveal that the ISS catalyst is more active than the WO₃ loaded catalysts, which is due to its higher surface area and surface acidity. Besides, the rate of the reaction is decreased with the increase of the WO₃ loading which may be due to the decrease of the surface area.

3.3.2. Effect of reaction temperature

Table 3 shows the influence of the reaction temperature on the esterification of PA with B, over the catalysts calcined at 400 °C, in the range of 70–110 °C using 0.20 g catalyst and molar ratio of PA:B = 1:2 for 4 h. The results indicate that the conversions of PA at 70 °C are low and increased gradually with the raising of the reaction temperature. The increase of the temperature brings more successful collisions which have sufficient energy (activation energy) to break the bonds and form products, resulting in higher values of PA conversion [20], and thus favor the formation of the ester [56]. It is also observed from Table 3 that the PA conversion over the catalysts calcined at 650 °C is much lower than the con-



Fig. 3. Change of PA conv.% with reaction time over the catalysts calcined at 400 °C.



Fig. 4. Kinetics of esterification of propionic acid with *n*-butanol over the catalysts calcined at 400 °C.

Table 2 Rate constants of the reaction over catalysts calcined at 400 $^\circ\text{C}.$

Catalyst	First order		Second order	
	k_1 (h ⁻¹)	R^2	k_2 , (M ⁻¹ h ⁻¹)	R^2
ISS	0.5761	0.9969	0.22165	0.9833
15 IWSS	0.4745	0.9944	0.18251	0.9887
35 IWSS	0.3772	0.9964	0.12213	0.9707

version over the400 °C products. The PA conversions at 90 °C are 22.45%, 8.51% and 9.91% over ISS-650, 15 IWSS-650 and 35 IWSS-650, respectively. The increase of reaction temperature to 110 °C causes a pronounced increase in PA conversion to attain 59.11%, 41.76% and 53.51%, respectively. The raising of the calcination temperature to 650 °C causes the loss of most Brønsted acid sites, the decomposition of sulfate ions and an increase in the crystallinity of the present phases, as a result decreases of both the surface acidity and the surface area of the catalysts (see Table 1). The Lewis acid sites at this calcination temperature are responsible mainly for the esterification of PA. These results are approved by increasing the WO₃ loading to 35 wt.% which are accompanied with an increase in the PA conversion that is due to the increase of the surface acidity and surface area of 35 IWSS-650 catalyst. Generally, the highest conversions are observed at the reaction temperature of 110 °C for both calcined products of 400 and 650 °C indicating that the reaction temperature of 110 °C is the optimum reaction temperature to the esterification of PA with B.

3.3.3. Effect of catalyst amount

The effect of the catalyst weight (0.05-0.30 g) on the esterification of PA with B over the 400 °C products is studied using the reactant molar ratio of PA:B = 1:2 at 110 °C for 4 h. The conversion of propionic acid results are given in Table 4, which indicate that the PA conversion is increased gradually with an increase in the weight of the catalyst. The PA conversion, however, over ISS and

Table 3

Effect of reaction temperature on PA conversion over the prepared catalysts.

Catalyst	Reaction temperature (°C)			
	70	80	90	110
ISS-400	23.88	32.06	47.99	78.54
15 IWSS-400	18.27	27.46	58.62	73.95
35 IWSS-400	12.14	27.46	36.84	71.97
ISS-650			22.45	59.11
15 IWSS-650			8.51	41.76
35 IWSS-650			9.91	53.51

Catalyst weight. 0.2 g; PA:B = 1:2; Reaction time 4 h.

35 IWSS catalysts has slightly increased when the catalyst weight is increased from 0.20 to 0.3 g. The increase of the catalyst weight means that there are more available active sites for this reaction.

3.3.4. Effect of reactant molar ratio

The influence of the reactant molar ratios on the PA conversion over the catalysts calcined at 400 °C is studied using 0.2 g of the catalyst at 110 °C for 4 h. The results for PA:B = 2:1, 1:1, 1:2 and 1:3 M ratios are shown in Table 5. It is clear that the increase of alcohol concentration to 1:1 leads to a remarkable increase in the PA conversion. Increasing the alcohol ratio further increases the conversion gradually to exhibit maximum at PA:B = 1:2. Generally, the increase of alcohol concentration of the ester. Furthermore, high initial amount of acid has a retarding effect on the esterification kinetics [57].

The decrease of the PA conversion may be explained on the basis of the fact that the increase in alcohol concentration hinders the esterification reaction by blocking the active sites on the catalyst surface [37,56] or dilution of propionic acid by excess alcohol. Thus, there is a competitive adsorption of the alcohol molecules on the acid sites with the acid molecules, which reduces the efficiency of the catalyst [37]. These obtained results are in good agreement with that observed on the esterification of PA with alcohols over Amberlyst 35 [19], a fibrous polymer-supported sulphonic acid (Smopex 101) [57] and PWS/ alumina catalysts [2]. The conversion of PA with *n*-butanol over the catalysts prepared in this work reach 62.5–70.40%, which are higher than that converted over cation exchange resins and HZSM-5 zeolites catalysts (30–56%) applying the same reaction conditions (PA:B = 1:1 at 110 °C for 4 h).

Comparison of the values of S_{BET} , surface acidity and catalytic activity of the prepared catalysts with that prepared previously in our laboratory which contain the same ratios of sulfate ions

Table 4		
Effect of cataly	st weight on PA conversion over the catalysts calcined	at 400 °C.

Catalyst weight (g)	PA conversion (%)		
	ISS-400	15 IWSS-400	35 IWSS-400
0.05	36.66	57.09	37.68
0.10	69.35	62.71	55.05
0.20	78.54	73.95	71.97
0.30	82.12	82.63	75.99

Reaction temp. 110 °C; PA:B = 1:2; Reaction time 4 h.

Table 5

Effect of the molar ratio of reactants on PA conversion over the catalysts calcined at 400 $^\circ\text{C}.$

PA:B	PA conversion (%)			
	ISS	15 IWSS	35 IWSS	
2:1	38.94	41.55	39.41	
1:1	69.43	70.42	62.53	
1:2	78.54	73.95	71.97	
1:3	77.82	71.59	58.42	

Reaction temp. 110 °C; catalyst weight 0.2 g; Reaction time 4 h.

and WO₃, but without the support aging, namely, SS, 15 WSS and 35 WSS catalysts [23], indicate that a slight change in the preparation conditions may highly influence these properties. For instance, catalysts prepared without aging the support, the SS, 15 WSS and 35 WSS and calcined at 400 °C show the following: (i) The S_{BET} values of 131, 114 and 86.9 m²/g, (ii) The acid strengths (E_i values) of 435, 473 and 465 mV, (iii) The acid amounts of 0.110, 0.063 and 0.140 mmol/g, (iv) The PA conversions of 76.76%, 71.38% and 77.20%, at the reaction conditions of: AP:B = 1:2, 0.20 g catalyst at 90 °C for 4 h. Whereas, in this work for similar catalysts prepared with aging, namely, for ISS, 15 IWSS and 35 IWSS catalysts, the results (see Tables 1 and 3), indicate that the aging of the support causes a decrease in S_{BET} , acid strength and catalytic activity, but a sharp increase in the acid amount of the catalyst.

3.3.5. Reusability of the catalysts

The reusability of solid catalysts is one of their main advantages over liquid homogeneous catalysts, and it is very important aspect of any industrial process. For the same purpose, reusability of the prepared catalysts hereafter is tested. The catalyst after 4 h conversion reaction is separated by filtration, washed with distilled water, dried at 120 °C and reactivated by calcination at 400 °C for 4 h. The catalyst then reused in the esterification reaction at the same conditions, using 0.2 g catalyst and PA:B = 1:2 at 110 °C for 4 h. The PA conversion over ISS-400 catalyst for a second run has decreased to 59.11%, i.e. loss \sim 20%, whereas for 15 IWSS-400 and 35 IWSS-400 catalysts the PA conversion has decreased by $\sim 13\%$ to be 61.18% and 58.11%, respectively. Sulfur leaching or reaction with alcohol is a possible cause of the catalyst deactivation during multiple reaction cycles [58]. These observations were in agreement with the results observed on esterification reactions over some catalysts such as SO_4^{2-}/ZrO_2 [58–60], SAC-13 [18] and 20% H₃PW/ZrO₂ catalysts [61]. For example, the catalytic esterification of methanol with carboxylic acids over SAC-13 catalysts has decreased by 50-70% [18], whereas, the activity of esterification of oleic acid with ethanol over 20% H₃PW/ZrO₂ catalyst has decreased by \sim 50% after use in second time [61].

3.3.6. Mechanism of the reaction

The esterification reaction is a straightforward reaction and subject to general acid catalysis. It may occur over Brønsted solid acid [1,2,20] or over Lewis acid sites [24,61]. Many authors [37,62,63] have reported that both Brønsted and Lewis acid sites are responsible for catalyzing the esterification reactions. The results obtained from the prepared catalysts indicate that these catalysts possess both Brønsted and Lewis acidic sites, and these sites are active in the esterification of PA with B. The mechanism of the reaction follows a Rideal–Eley mechanism in which propionic acid molecules are adsorbed first on the active acid sites of the catalyst, Brønsted and Lewis acid sites, forming protonated propionic acid or carbocation intermediate, and then react with *n*-butanol molecules from the bulk liquid forming new adsorbed carbocation which lose water molecule leaving adsorbed *n*-butyl propionate carbocation on the active sites. The *n*-butyl propionate is then des-

orbed from the surface. The adsorption and protonation of PA or carbocation formation on the catalyst surface is assumed to be the rate-controlling step. Details of these mechanisms can be found in the literature [37,24,56,57].

4. Conclusions

Mixing SnO₂ hydrogel with 15 wt.% SO₄²⁻ causes an increase in S_{BET}. The S_{BET} values depend on the calcination temperature and WO₃ loading. The addition of sulfate ions and WO₃ hinder the crystallization of SnO₂. The catalysts possess very strong acid sites and contain both Brønsted and Lewis acid sites. The addition of sulfate and WO₃ loading enhances the surface acidity and increases the acid strength of the acid sites. The acid strength, amount of acid sites, and esterification of propionic acid with *n*-butanol are the highest for the products calcined at 400 °C. The aging step shows a very critical advantage over non-aged catalysts.

The catalytic activity increases with reaction time and catalyst weight, and it is maximum for PA:B ratio of 1:2. The reaction obeys first order kinetics equation with respect to PA concentration. Brønsted and Lewis acid sites are proved to be essential for catalytic activity in *n*-butyl propionate formation.

Acknowledgments

The authors would like to thank Dr. Nael G. Yasri, University of Aleppo (Syria), for language revision and for the technical assistance during the course of this research.

References

- [1] W.T. Liu, C.S. Tan, Ind. Eng. Chem. Res. 40 (2001) 3281–3286.
- [2] P. Sharma, S. Vyas, A. Patel, J. Mol. Catal. A: Chem. 214 (2004) 281-286.
- [3] K. Arata, Appl. Catal A: Gen. 146 (1996) 3-32.
- [4] M. Doble, A.K. Kruthiventi, Green Chemistry and Engineering, Academic Press, 2006.
- [5] K. Arata, Preparation of Superacidic Metal Oxides and Their Catalytic Action, in: S.D. Jackson, J.S.J. Hargreaves (Eds.), Metal Oxide Catalysis, vol. 2, Wiley-VCH, Weinheim, 2009. p. 665–704, Chapter 17.
- [6] I. Arends, R. Sheldon, U. Hanefeld, Green Chemistry and Catalysis, Wiley-VCH, Weinheim, 2007.
- [7] A. Zheng, H.L. Zhang, L. Chen, Y. Yue, C.H. Ye, F. Deng, J. Phys. Chem. B 111 (2007) 3085–3089.
- [8] M. Hino, S. Takasaki, S. Furuta, H. Matsuhashi, K. Arata, Catal. Commun. 7 (2006) 162–165.
- [9] D. Fracasiu, K.H. Lee, J. Mol. Catal. A: Chem. 161 (2000) 213–221.
- [10] M. Hino, S. Takasaki, S. Furuta, M. Matsuhashi, K. Arata, Appl. Catal. A: Gen. 321 (2007) 147–154.
- [11] J.R. Sohn, S.H. Lee, J.S. Lim, Catal. Today 116 (2006) 143-150.
- [12] G.D. Yadav, G.S. Pathre, Micropor. Mesopore. Mater. 89 (2006) 16-24.
- [13] G.D. Yadav, G. George, Micropore. Mesopore. Mater. 96 (2006) 36-43.
- [14] K. Arata, H. Nakamora, M. Shouyi, Appl. Catal. A: Gen. 197 (2000) 213-219.
- [15] D.Q. Zhau, H. Yang, G.M. Dong, M.Y. Huang, Y.Y. Jiang, J. Mol. Catal. A: Chem. 159 (2000) 85–87.
- [16] J.R. Sohn, D.C. Shin, Appl. Catal. B: Environ. 77 (2008) 386–394.
- [17] Z. Ma, W.M. Hua, Y. Tang, Z. Gao, Chinese, Chem. Lett. 11 (2000) 87-88.
- [18] Y. Liu, E. Lotero Jr, J.G. Goodwin, J. Catal. 243 (2006) 221-228.
- [19] M.J. Lee, J.Y. Chiu, H. Lin, Ind. Eng. Chem. Res. 41 (2002) 2882-2887
- [20] S.H. Ali, A. Tarakmah, S.Q. Merchant, T. Al-Sahhaf, Chem. Eng. Sci. 62 (2007) 3197–3217.
- [21] N. Bahatt, A. Patel, J. Mol. Catal. A: Chem. 238 (2005) 223-228
- [22] J. Lilja, A. Aumo, T. Šalmi, D.Y. Murzin, P. Maki-Arvela, M. Sundell, K. Ekman, R. Peltonen, H. Vainio, Appl. Catal. A: Gen. 228 (2002) 253–267.
- [23] M.N. Alaya, M.A. Rabah, Arabian J. Chem (23 November 2012) (In press).
- [24] M.N. Alaya, M.A. Rabah, Arabian J. Chem. (13 October 2012) (In press).
- [25] A.I. Ahmed, S.A. El-Hakam, A.S. Khder, W.S. Abo El-Yazeed, J. Mol. Catal. A: Chem. 366 (2013) 99–108.
 [26] K. Tanabe, Solid Acid and Base Catalysts, in: J.R. Anderson, M. Boudart (Eds.),
- [20] K. Tahabe, Solid Acid and base Catalysis, In. J.K. Anderson, M. boudart (Eds.), Catalysis Science and Technology, vol. 2, Springer, Verlag, Berlin, Heidelberg and New York, 1981. Chapter 5, pp. 231–273.
- [27] R. Richards, Surface and Nanomolecular Catalysis, Taylor and Francis Group, London, 2006.
- [28] D.R. Fernandes, A.S. Rocha, E.F. Mai, C.J.A. Mota, V.T. da Silva, Appl. Catal. A: Gen. 425–426 (2012) 199–204.
- [29] A.C. Bose, D. Kalpana, P. Thangadurai, S. Ramasamy, J. Power Sources 107 (2002) 138–141.

- [30] I. Lu, Y. Liu, M. Dong, X. Wang, Sensor. Actuat. B 66 (2000) 225-227.
- [31] R.D. Sakhare, G.D. Khuspe, S.T. Navale, R.N. Mulik, M.A. Chougule, R.C. Pawar,
- C.S. Lee, S. Sen, V.B. Patil, J. Alloys Comp. 263 (2013) 300–306. [32] Q.Q. Wang, B.Z. Lin, B.H. Xu, X.L. Li, Z.J. Chen, X.T. Pian, Micropore. Mesopore.
- Mater. 130 (2010) 344–351. [33] Z. Chen, Y. Tian, S. Li, H. Zheng, W. Zhang, J. Alloys Comp. 515 (2012) 57–62.
- [34] C. Karuakaran, S.S. Raadha, P. Gomathisankar, J. Alloys Comp. 549 (2013) 269-275.
- [35] A. Sharma, M. Tomar, V. Gupta, Sens. Actuators B: Chem. 176 (2013) 143-151.
- [36] Y. Teraoka, T. Harada, T. Iwasaki, T. Ikeda, S. Kagawa, Chem. Lett. 22 (1993) 773-776.
- [37] A.S. Khder, E.A. El-Sharkawy, S.A. El-Hakam, A.I. Ahmed, Catal. Commun. 9 (2008) 769–777.
- [38] M. Hino, K. Arata, Bull. Chem. Soc. Japan 67 (1994) 1472-1474.
- [39] W. Xie, T. Wang, Fuel Process. Technol. 109 (2013) 150-155.
- [40] A.R. Khder, H.M.A. Hassan, M.S. El-Shall, Appl. Catal. A: Gen. 411-412 (2012) 77-86.
- [41] M.N. Alaya, M. Rabah, Res, J. Aleppo Univ. Basic Sci. Ser. 61 (2008) 13-36.
- [42] M.N. Alaya, M. Karman, H. Hello, Res, J. Aleppo Univ. Basic Sci. Ser. 62 (2008) 13–38.
- [43] T. Yamaguchi, Appl. Catal. 61 (1990) 1–25.
- [44] Z. Ma, W.M. Hua, Y. Tang, Z. Gao, J. Mol. Catal. A: Chem. 159 (2000) 335–345.
 [45] G.M. Maksimov, M.A. Fedotov, S.V. Bogdanov, G.S. Litvak, A.V. Golovin, V.A.
- Likholobov, J. Mol. Catal. A: Chem. 158 (2000) 435-438.
- [46] H. Matsuhashi, H. Miyazaki, K. Arata, Chem. Lett. 30 (2001) 452–453.
 [47] H. Matsuhashi, H. Miyazaki, T. Kawamura, H. Nakamura, K. Arata, Chem. Mater. 13 (2001) 3038–3042.

- [48] P. Villabrille, P. Vazques, M. Blanco, C. Caceres, J. Colloid Interf. Sci. 251 (2002) 151–159.
- [49] E.A. El-Sharkawy, A.S. Khder, A.I. Ahmed, Micropore. Mesopore. Mater. 102 (2007) 128–137.
- [50] A.S. Khder, A.I. Ahmed, Appl. Catal. A: Gen. 354 (2009) 153-160.
- [51] L.R. Pizzio, P.G. Vazquez, C.V. Caceres, M.N. Blanco, Appl. Catal. A: Gen. 256 (2003) 125–139.
 [52] B. Tyagi, M.K. Mishra, A. Tasra, J. Mol. Catal. A: Chem. 301 (2009)
- 67-78. [53] K.N. Rao, K.M. Reddy, N. Lingaiah, I. Suryanarayana, P.S.S. Prasad, Appl. Catal.
- A: Gen. 300 (2006) 139–146. [54] S. Furata, H. Matsuhashi, K. Arata, Appl. Catal. A: Gen. 269 (2004)
- 187-191.
- [55] S.R. Kirumakki, N. Nagaraju, K.V.R. Chary, Appl. Catal. A: Gen. 299 (2006) 185– 192.
- [56] A.S. Khder, Appl. Catal. A: Gen. 343 (2008) 109–116.
- [57] J. Lilja, J. Warna, T. Salmi, LJ. Pettersson, J. Ahlkvist, H. Grenman, M. Ronnholm, D.Y. Murzin, Chem. Eng. J. 115 (2005) 1–12.
- [58] D.E. Lopez Jr, J.G. Goodwin, D.A. Brunce, S. Furuta, Appl. Catal. A: Gen. 339 (2008) 76–83.
- [59] A. Corma, H. Garcia, Catal. Today 38 (1997) 257–308.
- [60] F. Omota, A.C. Dimian, A. Bliek, Chem. Eng. Sci. 58 (2003) 3175-3185.
- [61] C.F. Oliveira, L.M. Dezaneti, F.A.C. Garcia, J.L. De Macedo, J.A. Dias, S.C.L. Dias, K.S.P. Alvim, Appl. Catal. A: Gen. 372 (2010) 153–161.
- [62] S.L. Barabosa, M.J. Dabdoub, G.R. Huratado, S.I. Klein, A.C.M. Baroni, C. Cunha, Appl. Catal. A: Gen. 313 (2006) 146–150.
- [63] S.K. Samantaray, K. Parida, React. Kinet. Catal. Lett. 78 (2003) 381-387.