Sucrose-mediated sol–gel synthesis of nanosized pure and S-doped zirconia and its catalytic activity for the synthesis of acetyl salicylic acid

Ali Majedi a, Fatemeh Davar b,*, Alireza Abbasi a

a School of Chemistry, College of Science, University of Tehran, Tehran, Islamic Republic of Iran
b Department of Chemistry, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

1. Introduction

Bronsted–Lewis acids are catalyzed for many organic chemical reactions such as Friedel–Crafts alkylation [1], esterification [2] and alcohol dehydration [3]. Homogenous based acids like sulfuric acid or phosphoric acid have limited industrial applications due to the difficult and costly catalyst separation and recovery as well as the corrosion of the equipment used [4]. Solid heterogeneous catalysts are used to overcome these problems because they are noncorrosive, non-toxic, and easily separated for recycling, so they are ‘green’ catalysts. However, their relatively small surface areas often limit the activities and confine its wide application in catalytic reactions [5]. One of the best techniques used to increase the surface area of solid catalysts is nano-crystallization [6,7]. Zirconia and modified zirconia with anions such as sulfate ions are interesting solid acids because they form highly acidic or super acidic properties [8,9]. For the preparation of nano-crystalline zirconia, the sol–gel technique has been adopted as a versatile method, since this method is a solution process that allows flexibility in the parameter control due to its relatively slow reaction process. This permits tailoring of certain desired structural characteristics such as composition, homogeneity, grain size, particle morphology and porosity [10,11]. Recently Reddy et al. review almost all reactions that have ever been reported in the presence of zirconia-based solid acids include drug synthesis [12]. Acetyl salicylic acid, also known as aspirin, is a salicylate drug often used as an analgesic to relieve minor aches and pains; it is also taken as an antipyretic to reduce fever, and as an anti-inflammatory medication. Aspirin in the body also has an anti-thrombotic function, effectively inhibiting the aggregation of blood platelets. It has been widely used for the prevention and treatment of cardiovascular and cerebrovascular diseases [13]. Acetyl salicylic acid is commercially prepared by an acetylation reaction with salicylic acid and acetic anhydride in the presence of concentrated H₂SO₄ or H₃PO₄ at 80–90 °C [14]. Table 1 shows the yield of acetylsalicylic acid obtained by using some different solid acids. This article represents a simple method for synthesizing pure and S-doped ZrO₂ by the sucrose mediated sol–gel procedure with a zirconium(IV) acetylacetonate precur- sors and thiourea as a sulfur source. There are few reports on synthesizing zirconia nanoparticles using the sucrose mediated sol–gel procedure with a zirconium(IV) acetylacetonate precursor and thiourea as a sulfur source. There are several reports on synthesizing zirconia nanoparticles using the sucrose mediated sol–gel method in an acidic environment [17,18], but no works in basic conditions have been done. Hence the as prepared samples were characterized with different techniques, the proposed technique for the formation of zirconia nanoparticles in this situation will be discussed and the efficiency of the samples as the solid acid catalyst was evaluated in the acetyl salicylic acid synthesis. The acetyl salicylic acid was synthesized by pure and S-doped zirconia as a heterogeneous acid catalyst according to (Scheme 1).

ARTICLE INFO

Article history:
Received 14 December 2013
Accepted 6 January 2014
Available online 22 January 2014

Keywords:
Sol–gel
Zirconia
Nanoparticle
Acetyl salicylic acid
Heterogeneous catalyst

ABSTRACT

Nano-sized pure and S-doped zirconia was prepared by the sol–gel method in the presence of sucrose and zirconium(IV) acetylacetonate (Zr(acac)₄) as a gelation agent and Zr⁴⁺ source, respectively. Acid catalyst activity of samples was tested for the production of acetyl salicylic acid from salicylic acid and acetic anhydride as precursors, The yield (64.0%) of acetylsalicylic acid was obtained from 50 mg of S-doped zirconia calcined at 550 °C and after a 3 h reaction, was comparably higher than the yield of the reaction (13.3%) in the absence of a catalyst and under the same reaction condition.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
Table 1

Yield (wt.%) of acetylsalicylic acid (ASA) over various solid acid catalysts.

<table>
<thead>
<tr>
<th>Solid acid name</th>
<th>Reaction conditions</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naβ</td>
<td>a</td>
<td>16</td>
<td>[15]</td>
</tr>
<tr>
<td>NaY</td>
<td>a</td>
<td>10</td>
<td>[15]</td>
</tr>
<tr>
<td>NaZSM5</td>
<td>a</td>
<td>13</td>
<td>[15]</td>
</tr>
<tr>
<td>Hβ</td>
<td>a</td>
<td>76</td>
<td>[15]</td>
</tr>
<tr>
<td>HYO</td>
<td>a</td>
<td>65</td>
<td>[15]</td>
</tr>
<tr>
<td>HZSM5</td>
<td>a</td>
<td>71</td>
<td>[15]</td>
</tr>
<tr>
<td>Pt-Hβ</td>
<td>a</td>
<td>98</td>
<td>[15]</td>
</tr>
<tr>
<td>Pt-HY</td>
<td>a</td>
<td>86</td>
<td>[15]</td>
</tr>
<tr>
<td>Pt-HZSM5</td>
<td>a</td>
<td>92</td>
<td>[15]</td>
</tr>
<tr>
<td>Sulfated titania</td>
<td>b</td>
<td>92–95</td>
<td>[16]</td>
</tr>
<tr>
<td>Sulfated zirconia</td>
<td>b</td>
<td>80–85</td>
<td>[16]</td>
</tr>
<tr>
<td>Hβ</td>
<td>b</td>
<td>83–85</td>
<td>[16]</td>
</tr>
<tr>
<td>HY</td>
<td>b</td>
<td>78–79</td>
<td>[16]</td>
</tr>
<tr>
<td>HZSM5</td>
<td>b</td>
<td>70–75</td>
<td>[16]</td>
</tr>
<tr>
<td>K-10</td>
<td>b</td>
<td>65–69</td>
<td>[16]</td>
</tr>
</tbody>
</table>

a = salicylic acid = 1 g, acetic anhydride = 3 g, catalyst = 0.05 g, reaction temp: 120 °C, and time: 45 min.
b = salicylic acid = 1 g, acetic anhydride = 3 g, catalyst = 0.1 g, reaction temp: 120 °C, and time: 30 min.

2. Experimental

2.1. Materials and physical measurement

The zirconium (IV) Acetylacetonate, sucrose, ammonia, Thiourea, ethanol and acetic anhydride were purchased from the Merck Company. The Salicylic acid was purchase from Dae-Jung Reagent Chemicals CO. Ltd. All chemicals were used without further purification. TG/DTA analysis was carried out using a simultaneous thermal analysis instrument (NETZSCH STA 409 PC/PG) with a flow rate of 20.0 ml min⁻¹ and a heating rate of 10 °C min⁻¹. XRD patterns were recorded on a Philips Xpert Pro MPD model X-ray diffractometer using Cu Ka radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 20–80°. Field emission scanning electron microscopy (FE-SEM) images were obtained by Hitachi (Japan), FT-IR spectra of the samples were recorded on a Nicolet Magna IR 550 spectrometer. The UV-Vis absorbance spectra was obtained for the samples using spectro UV-Vis double beam PC scanning spectrophotometer model UVD-2950 equipped with glass of 1 cm path length and the spectra was recorded at room temperature in air within the range 200–600 nm.

2.2. Preparation of ZrO₂ nanoparticles

Zirconia and S-doped zirconia nanoparticles were prepared from a zirconium(IV) acetylacetonate precursor Zr(acac)₄ [acac = CH₃-C(O)CH(O)CH₃]. Initially, 2 mmol Zr(acac)₄ was dissolved with 30 ml ethanol at 70 °C, and then sucrose was added to the solution; the solution was stirred for 30 min using a magnetic stirrer. After that, hydrolyzation started to take place due to drop-by-drop addition of distilled water containing ammonia (alkaline condition, pH ~ 12). The resulting milky white gel was stirred for one more hour and dried at 110 °C; subsequently, the resulting material was powdered and then calcined in a muffle furnace at different temperatures for 2 h (490, 550 and 650 °C). For the preparation of nano sulfated zirconia, thiourea (0.1 mmol) was dissolved in 30 ml of distilled water and the above steps were repeated. Scheme 2 shows procedure steps followed for the preparation of pure and S-doped zirconia.

2.3. Synthesis of acetylsalicylic acid

The typical procedure for acetylsalicylic acid synthesis has been mentioned in Ref. [19] with a few variations: The acetylation of salicylic acid with acetic anhydride was conducted in a 50 mL batch reactor equipped with magnetic agitation. Typically, 1 g salicylic acid, 3 mL acetic anhydride and 50 mg of a prepared catalyst were taken in the reactor. The catalyst was separated by the centrifugation at reaction temperature. Aliquots of the mixture were taken and unreacted acetic anhydride was hydrolyzed to acetic acid by adding water (10 ml), and slowly cooled to room temperature in an icy water bath without agitation to obtain white acetylsalicylic acid crystals. Then the crystals were collected by filtration, and washed with chilled water to obtain acetylsalicylic acid. The crude crystals were purified by re-crystallization in an ethanol–water solution. The crystal was confirmed to be acetylsalicylic acid due to the melting point, as measured by FT-IR and phenol test. The yield of the re-crystallized pure products was calculated as follows:

\[
\text{Yield (wt.%)} = \frac{\text{obtained wt. of product}}{\text{theoretical wt. of product}} \times 100
\]

2.4. Catalyst regeneration

Catalyst deactivation is a problem of great technical, economic and ecologic concern in the practice of industrial chemical processes. One of the main reason for deactivation is attributed to poisoning of the acid active on substance by the organic absorption [20]. To study the regeneration and reuse of the catalyst, a catalyst was recovered from the reaction mixture by centrifugation and washed with acetone. This was followed by drying at 110 °C for 1 h and thermal activation at 450 °C for 1 h. The absorbed organic species can be burned out at high temperature to regenerate catalytic activity. The regenerated catalyst was studied for the synthesis of acetyl salicylic acid under similar reaction conditions; after every reaction cycle, the catalyst was recovered, washed and activated as explained above. Moreover, for comparison of catalytic activity of nanosized zirconia with its microsized bulk, the one sample was prepared with Pulse Electrical Explosion (PEE) Nano Engineering and Manufacturing Co. (Model: PEE10k or PEE50K (Nano Engineering and Manufacturing Co. (PNF Co.), made in Iran).

3. Results and discussion

3.1. X-ray diffraction and phase structure

At atmospheric pressure, pure zirconia has three solid polymorphs which exhibit monoclinic structure [space group...
P21/c (m-phase), that is thermodynamically stable at the temperatures below 1172 °C, tetragonal structure [space group P42/nmc] (t-phase), stable at the temperature range of 1172–2347 °C, and cubic structure [space group Fm3m] (c-phase), stable above 2347 °C. However, nano zirconia powders are often yield tetragonal or cubic polymorphs, because of surface energy differences between polymorphs [21]. Among different polymorph of zirconia, tetragonal phase shows more effective catalyst.

Scheme 2. Diagram illustration of step procedure for preparation of pure and S-doped zirconia nanoparticles.

Fig. 1. XRD patterns of pure ZrO₂ calcined at: (a) 490 °C, (b) 550 °C, (c) 650 °C and S-doped ZrO₂ calcined at: (d) 550 °C and (e) 650 °C.
property than other polymorphs [22]. In order to investigate the
temperature effects and S-doping on the crystallization process of
zirconia, XRD results of pure and S-doped zirconia, calcined at
650 °C, 540 °C and 490 °C for 2 h were compared.

Fig. 1a and d shows XRD pattern of pure and S-doped zirconia
calculated at 490 °C respectively. The nanocrystalline tetragonal
structure was confirmed by 2θ = 30.32°, 34.9°, 50.6° and 60.08°
correspond to (1 0 1), (0 0 2), (2 0 0) and (2 1 1) reflections. So, XRD
patterns of as-prepared samples calcined at 490 °C was indexed as
t-phase of zirconia which is in good agreement with the reported
data (JCPDS No. 01-080-2155). The tetragonal structure can be
obtained from the cubic structure wherein one of the axes of the
cubic fluorite structure is elongated and correspondingly oxygen
anions are displaced from their ideal positions along the direction
of elongation. This is observed as splitting of some of the XRD
peaks. The literature [23,24] reported that the tetragonal structure
is elongated and correspondingly oxygen
anions are displaced from their ideal positions along the direction
of elongation. This is observed as splitting of some of the XRD
peaks. The literature [23,24] reported that the tetragonal structure
can be distinguished from the cubic structure in the presence of
characteristic splitting of the tetragonal phase, such as (0 0 2)/
(1 1 3)/(3 1 1) and (0 0 4)/(4 0 0) at 2θ = 35.11, 60.021 and
73.41, respectively, whereas the cubic phase exhibits only single
peaks at all of these positions. All of XRD patterns of pure and S-
doped zirconia show splitting peak at this position. So, it was
concluded that no cubic phase of ZrO2 was obtained for all samples.

The main peaks of monoclinic phases were at 2θ = 28.23 (1 1 1)
plane and 2θ = 31.61 (1 1 1) planes. These peaks appear in Pure and
S-doped zirconia calcined at 650 °C (Fig. 1c and f). This figure
indicates that a mixture of monoclinic (m) and tetragonal (t) phase
of zirconia was obtained at this temperature. The volume fractions
of monoclinic and tetragonal phases of the zirconia were
determined using the following correlations in this equation [25]:

\[ \nu_m = \frac{1.311X_m}{1 + 0.311X_m} \]

where \( \nu_m \) is the volume fraction of the monoclinic phase and \( X_m \)
is given by:

\[ X_m = \frac{I_m(\bar{1} 1 1) + I_m(1 1 1)}{I_m(1 1 1) + I_m(1 1 1) + I_t(0 1 0)} \]

Setting the value for pure zirconia and doped zirconia calcined
at 650 °C give a 20.07% and a 17.20% monoclinic phase,
respectively. These results showed that monoclinic phase forma-
tion was affected by sulfur addition due to the restriction in the
crystallite growth, which was imposed by the dopants.

Table 2
Crystal phase and crystal size of as prepared samples main peaks.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>2θ (°)</th>
<th>FWHM</th>
<th>Crystal size</th>
<th>Phase</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.32</td>
<td>0.246</td>
<td>33.5</td>
<td>t</td>
<td>490</td>
</tr>
<tr>
<td></td>
<td>50.31</td>
<td>0.688</td>
<td>12.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60.39</td>
<td>0.688</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30.31</td>
<td>0.344</td>
<td>23.9</td>
<td>t</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>50.73</td>
<td>0.246</td>
<td>35.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>62.72</td>
<td>0.393</td>
<td>23.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30.39</td>
<td>0.5412</td>
<td>15.2</td>
<td>t, m</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>50.41</td>
<td>0.393</td>
<td>22.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60.41</td>
<td>0.295</td>
<td>31.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>30.38</td>
<td>0.231</td>
<td>35.8</td>
<td>t</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>50.31</td>
<td>0.246</td>
<td>35.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60.32</td>
<td>0.427</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>29.63</td>
<td>0.344</td>
<td>23.9</td>
<td>t, m</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>50.29</td>
<td>0.295</td>
<td>29.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>59.73</td>
<td>0.246</td>
<td>37.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2. Thermal analysis

Fig. 2 shows the TG–DTA analysis of pure and S-doped zirconia powders before calcination. A little weight loss could be observed in the range of 100–300 °C, probably due to dehydration. It was followed by an endothermic peak (energy used to release volatile compounds). An exothermic peak followed by great weight loss nearly 43% at 300–600 °C was observed. This is the typical behavior for the combustion of organic compounds [27]. The loss continued till 650 °C, showing that organic compounds could exist till 650 °C, as confirmed by FT-IR. Starting from 650 °C up to 1000 °C, the samples display weight loss less than 10% could be attributed to carbon residue in the samples. Also an endothermic peak about 840 °C could be observed, this may be assigned to t-m phase transformation [28,35].

3.3. Field emission scanning electron microscopy (FESEM) analysis

Fig. 3 shows FESEM micrographs of the zirconia and S-doped zirconia samples at different temperatures. Images show that nanoparticles are uniform, quasi spherical particles. The particle size histogram of the prepared particles at different temperature was obtained from 70 observed nanoparticles (Fig. 4). The histogram of pure zirconia calcined at 490 °C shows the particles with a 27.98 nm average value and a 5.3 nm standard deviation (Fig. 4a). As the calcination temperature of the prepared pure zirconia increased to 550 °C the particle size increases to a 28.93 nm average value and particle size distribution decreases to a 3.26 nm (Fig. 4b). It is believed that with increasing temperature, the diffusion rate increased, and this will speed up the coalescence process between neighboring ‘grains’ and hence producing larger structures. Pure zirconia calcined at 650 °C particle size has a 27.16 nm average value and a 4.8 nm standard deviation (Fig. 4c). This decreased average value by increasing the temperature probably is occurred due to monoclinic phase transformation. Fig. 4d and e shows the average values of 26.53, 28.83 and 28.93 nm for S-doped zirconia calcined at 490 °C, 550 °C and 650 °C respectively. These values are different from values obtained by pure zirconia. In general, grain growth or crystallite growth in ZrO2 is considerably affected by the dopant. Little crystallite growth was observed in S-doped ZrO2. Thermodynamic stability of tetragonal phase compared to monoclinic phase in smaller crystallites is a well-known phenomenon [29] and hence the increased stability of the tetragonal phase observed here is due to the restriction in crystallite growth imposed by dopant.

3.4. FT-IR spectroscopy analysis

Fig. 5 shows FT-IR spectra of pure and S-doped zirconia calcined at different temperatures. All samples showed peaks corresponding
Fig. 4. The histograms obtained from corresponded FESEM images of pure ZrO$_2$ calcined at: (a) 490 °C, (b) 550 °C, (c) 650 °C and S-doped ZrO$_2$ calcined at: (d) 490 °C (e) 550 °C and (f) 650 °C.

Fig. 5. FT-IR spectra of pure zirconia calcined at: (a) 490 °C, (b) 550 °C, (c) 650 °C and S-doped ZrO$_2$ calcined at: (d) 490 °C (e) 550 °C and (f) 650 °C.
to stretching vibrations of the O–H and bending vibrations of the adsorbed water molecules at about 3350–3450 cm$^{-1}$ and 1620–1635 cm$^{-1}$, respectively. Two extremely weak peaks that appeared at 2854 and 2922 cm$^{-1}$ were attributed to the C–H stretching models and peak bands centered at 1450 and 1100 cm$^{-1}$ were assigned to the bending vibrations of C–H bonds in the species linking. The C–H bond was related to the carbon chain of the organic additives adsorbed on the Zirconia surface. For pure samples calcined at 490 °C (Fig. 4a), a broad band with a peak at 542 cm$^{-1}$ and a shoulder at 627 cm$^{-1}$ were ascribed to Zr–O vibrations of t-ZrO$_2$. For pure zirconia, samples were calcined at 550 °C and 650 °C (Fig. 4b and c). The sharp band at 746 cm$^{-1}$ was the characteristic of m-ZrO$_2$. A similar observation was reported by Chen et al. [30] for zirconia nanoparticles. For the S-doped zirconia, Fig. 4d–f shows additional peaks at 1116 and 1383 cm$^{-1}$, which were related to sulfated ions assigned to asymmetric and symmetric stretching frequency of S–O and S–O bonds. These are characteristic of inorganic chelating bidentate sulfates [31]. S-doped zirconia samples calcined at 490 °C and 550 °C had no peak at 746 cm$^{-1}$ although this peak appeared at 650 °C, indicating that the dopant prohibited the monoclinic formation at 550 °C.

3.5. UV–vis absorption spectra

Fig. 6 displays the UV–vis absorption spectra of the obtained pure and doped ZrO$_2$ nanocrystals calcined at different temperatures. All the samples showed a sharp peak about 212 nm (5.8 eV). It is well known that ZrO$_2$ is a direct band gap insulator with two band-to-band transitions and this peak is attributed to the band gap energy of zirconia. The obtained data agreed with that found by Xu et al. [32]. Apart from the strong absorption peak, a shoulder about 230 nm (5.39 eV) and a weak peak was centered at 287 nm (4.3 eV) is observed. This peak was expected to arise from transitions involving extrinsic states such as surface trap states, defect states or impurities [33]. Because the configuration of Zr$^{4+}$ ions is d$^0$, no features characteristic of d → d transition was found in the vision region (400–600 nm). There were no significant differences between pure and S-doped, indicating that sulfur doping did not change the crystal structure of zirconia [34].

3.6. Mechanism of zirconia nanoparticles formation

The first step in the formation of pure and S-doped zirconia nanoparticle took place by a nucleophilic attack of the OH$^-$ on the central Zr atom according to a SN2 mechanism (Scheme 3a). The nature of chelating ligands are noticeably changes the rate of hydrolysis-polycondensation [35]. Acetylacetonate ligand could exist in two tautomeric enol-keto forms that rapidly were interconverted although the keto form was more stable in a polar solvent such as water. Such a ligand is a good hydrolysable ligand that could be accelerating sol formation (Scheme 3b) [36].
Polycondensation results in the formation of nanoscale clusters of metal oxides or hydroxides. According to the literature, sucrose and sucrose degradation products act as chelating agents for metal cations, templating agents, and fuel for combustion [37]. In this process, sucrose was used as a gel agent to keep Zr(OH)\textsubscript{4} in a homogeneous solution with hydrogen bonding (Scheme 3c). With temperatures rising to 110°C, polycondensation took place; in an alkaline medium at about 100°C, sucrose could slightly hydrolyze to water soluble products: hydroxyacetone, acetic acid, propionic acid, 2-hydroxy-3-methyl-2-cyclopentene-1-one, 2–5-dimethyl-1,4hydroxy3 (2H) furane and lactic acid [38]. The presence of sucrose along with these products could also increase the viscosity of sol and reduce the rate of crystallization of ZrO\textsubscript{2} nanoparticles, thereby favoring the formation of less agglomerated zirconia. Sucrose was decomposed exothermally at a low ignition temperature (480°C), leaving behind only a small amount of carbon residue [39].

The overall reaction of nanocrystalline zirconia from Zr(acac)\textsubscript{4} could be written as follows:

\[
\text{Zr(C}_5\text{H}_7\text{O}_2\text{)}\textsubscript{4} + \text{C}_1\text{2H}_{22}\text{O}_{11} + 2\text{NH}_4\text{OH} + 17/2\text{O}_2 \xrightarrow{T \geq 490} \text{ZrO}_2 + \text{NO}_2 + \text{CO}_2 + 30\text{H}_2\text{O}
\]

### 3.7. Catalytic Activity

Table 3 shows the yield of acetyl salicylic acid from the O-acetylation of salicylic acid with acetic anhydride using nanocrystalline, pure and S-doped prepared zirconia for 1 h after the reaction took place. According to Table 3, the catalytic activities were observed in the following order: 6 > 5 > 2 > 3 > 7 > 4 > 1. To summarize, the catalyst particles calcined at 650°C had a small monoclinic phase, thereby showing a lower yield although the S-doping increased the yield. The observed trend could be explained in terms of acidity and the textual properties of the solid acid catalysts. To investigate how time changed the yield of acetyl salicylic acid, the experiment was carried out with a sulfated zirconia catalyst calcined at 550°C; it was chosen because it had a greater yield expectancy and the reaction times were in increments of 60 min until 180 min. Table 4 shows that an increase in the time resulted in an increase in the yield of acetyl salicylic acid from 47.1 to 64 wt.%. Then the prepared sulfated zirconia catalyst calcined at 550°C was re-used for 3 reaction cycles and washed, dried and calcined at 450°C for 1 h. The thermally regenerated catalyst was used for the next reaction cycle and the result (Table 5) gave a similar yield of acetyl salicylic acid as the fresh catalyst. This clearly indicated that the

### Table 3

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Catalyst</th>
<th>Acetyl salicylic acid (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without catalyst</td>
<td>9.8</td>
</tr>
<tr>
<td>2</td>
<td>Pure zirconia calcined at 490°C</td>
<td>37.3</td>
</tr>
<tr>
<td>3</td>
<td>Pure zirconia calcined at 550°C</td>
<td>36.4</td>
</tr>
<tr>
<td>4</td>
<td>Pure zirconia calcined at 650°C</td>
<td>27.3</td>
</tr>
<tr>
<td>5</td>
<td>S-doped zirconia calcined at 490°C</td>
<td>46.2</td>
</tr>
<tr>
<td>6</td>
<td>S-doped zirconia calcined at 550°C</td>
<td>47.1</td>
</tr>
<tr>
<td>7</td>
<td>S-doped zirconia calcined at 650°C</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Reaction condition: time 1 h, salicylic acid 1 g, acetic anhydride 3 ml, 50 mg prepared catalyst, temperature 80°C.

### Table 4

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Acetyl salicylic acid (wt.%) Without catalyst</th>
<th>Acetyl salicylic acid (wt.%) S-doped zirconia catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.8</td>
<td>47.1</td>
</tr>
<tr>
<td>2</td>
<td>11.4</td>
<td>56.3</td>
</tr>
<tr>
<td>3</td>
<td>13.3</td>
<td>64.0</td>
</tr>
</tbody>
</table>

Reaction condition: salicylic acid 1 g, acetic anhydride 3 ml, temperature 80°C.
Table 5

<table>
<thead>
<tr>
<th>Catalyst reuse</th>
<th>Acetyl salicylic acid (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>63.4</td>
</tr>
<tr>
<td>3</td>
<td>62.3</td>
</tr>
</tbody>
</table>

Reaction condition: time 3 h, salicylic acid 1 g, acetic anhydride 3 ml, 50 mg prepared catalyst, temperature 80°C.

![Salicylic acid reaction](image)

**Scheme 4.** Salicylic acid indication with FeCl₃.

deactivation of catalysts was attributed to the absorption of the organic substance on the active sites. The absorbed organic species could be burned.

3.8. Characterization of the synthesized acetyl salicylic acid

The obtained acetyl salicylic acid from the catalytic reaction was re-crystallized with an ethanol/water mixture and characterized by its melting point, FT-IR and a phenol test. Phenols, like salicylic acid, reacted with FeCl₃ (aq) to give a deep purple complex. Phenol was not present in this product, but it was one of the reactants. This test indicated the presence of an unreacted starting material (Scheme 4). Results in all samples showed that the melting point of 136°C accommodated the melting point of pure acetyl salicylic acid. FT-IR (KBr) peak at 3491 cm⁻¹ νOH (–COOH), 1755 cm⁻¹ νC=O (–COOCH₃), and 1690 cm⁻¹ νC=O (–COO) confirmed the acetyl salicylic acid formation. Phenol test showed that no purple coloring of salicylic acid existed in the products.

4. Conclusion

Nanosized pure and S-doped zirconia nanoparticles were synthesized in one pot simple sol–gel method mediated with sucrose. Sucrose created complexes with the sol of zirconia and acts as a gelation agent and templates the zirconia sol; after that, sucrose decomposition at calcination temperature generated excess heat and gases that favoring the formation of less agglomerated zirconia and improve the surface area of the final product. SEM micrographs of the pure and S-doped zirconia samples at different temperatures showed uniform, quasi spherical particles with particle sizes of 18–49 nm. The XRD results revealed that the pure zirconia nanocatalyst calcined at 490°C had a tetragonal phase; with increasing temperatures to 650°C, 20.07% monoclinic phase was also obtained. The XRD results showed S-doped zirconia's tetragonal phase at 490°C, and a 17.2% monoclinic phase appeared at 650°C. XRD diffraction of both pure and S-doped zirconia calcined at 550°C showed no peaks from the monoclinic phase. However, IR spectra of pure zirconia at 550°C showed a characteristic peak of m-ZrO₂ that was too small to be detectable in XRD. This proposed that the sulfur dopant affected the phase transformation at 550°C. Also, the FT-IR spectra confirmed the presence of sulfated ions in S-doped zirconia. Acid catalysis reactions during the synthesis of acetyl salicylic acid showed that S-doped zirconia nanoparticles calcined at 550°C had higher activities than other catalyst samples and the yield of 64% was obtained from acetyl salicylic acid synthesized after 3 h from the reaction start. The catalytic properties of S-doped catalysts were maintained throughout the three successive reactions. Other characterizations proved that the catalytic activity highly depended on S-doping of zirconia, possibly due to the higher acidity promoted by the sulfur in the catalysts.

References

(b) M. Salavati-Niasari, M. Dadkhah, F. Davar, Polyhedron 28 (2009) 3005;