Stannous chloride (SnCl₂) and stannous sulfate (SnSO₄) synthesis from tin powderization waste

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Abstract. The necessity of finding a way to utilize Sn metal from tin powderization waste as effectively and efficiently as possible has risen because of the large number of industrial by-products of Sn waste and the broad applications of tin chemicals in the world. Stannous chloride (SnCl₂) and stannous sulfate (SnSO₄) are tin-derived compounds in which their applications are in various fields, and one of which is catalysts. Catalyst products produced from the two compounds are STO (Sulfated Tin Oxide) catalyst. In this study, tin powderization waste was used as raw material for the synthesis of SnCl₂ and SnSO₄. The purpose of using tin waste is an effort to create the Sustainable Development Goals (SDG) program launched by the United Nations to obtain a sustainable consumption and production system. Tin powder from the off-spec product of the tin powderization process can be used as raw material to manufacture tin-derived chemical compounds. Overall, the process of developing tin products will produce a non-waste system (zero waste). The optimum conditions to synthesize SnCl₂ are as follows; the tin powder particle size is 500 mesh with HCl 12 M at 80°C with a yield percentage of 95%. The synthesis of SnSO₄ with the reaction of SnCl₂ + (NH₄)₂SO₄ can be carried out using stirring techniques. The results of the FT-IR spectrometer showed a spectrum of sulfate groups in the region ~ 1181 cm⁻¹.

1. Introduction

Tin is one of the abundant natural resources in Indonesia. Indonesia's tin reserves are ranked second after China [1, 2]. In the 2015-2045 National Research Master Plan, mining materials' processing is one of the research priorities to increase Indonesia's economic contribution [3]. Tin derivative products are one of the critical components in the industrial sector. Around 16% of the total ingot produced will be processed into tin-derived compounds. Also, ingots are widely processed in the plating industry in solder (47%) and tin plates (15%). Other uses of tin include brass and bronze metal (5.5%), glass industry (2%), and other applications (11%). In general, the use of tin by industry varies significantly from heavy industry to daily needs industry. Tin production is commonly used in the tin plate industry, the coating industry, the solder industry, the bronze and buckling industry, the metal alloy industry, the coating industry for household needs, the food packaging industry, the electrical coating industry (electroplating), pharmaceutical product industry, agricultural equipment industry, ceramic industry, plastic industry, motor vehicle industry, electronics industry, thin steel coating industry, tin salt product industry, glaze dye industry in the ceramic industry and chemical industry for glass [4-6].
Stannous chloride (SnCl₂) and stannous sulfate (SnSO₄) is a tin-derived compound with applications in various fields, such as catalysts. One of the catalyst products developed from the two compounds is the STO (Sulfated Tin Oxide) catalyst [7-10]. Tin oxide (SnO₂) is a heterogeneous catalyst used in esterification reactions and various organic reactions [11]. From previous studies, the stability of heterogeneous catalysts influences the efficiency of these catalysts. The addition of anions, such as sulfate and phosphate, can increase surface acidity to increase catalyst activity [11].

In this study, tin powderization waste was used as raw material for the synthesis of SnCl₂ and SnSO₄ as precursors for STO catalysts. The use of this waste is an effort to realize the Sustainable Development Goals (SDG) program launched by the United Nations so that a sustainable consumption and production system can be obtained [12]. This waste treatment process follows the previously successful Zn waste treatment process [13]. The tin powder results that do not meet industry specifications can be used as raw material to manufacture tin-derived chemical compounds. Overall, the process of developing tin products will produce a non-waste system (zero waste).

2. Materials and methods

Tin powder from the tin powderization process's off-spec product was sieved into three size variations, 200, 400, and 500 mesh. SnCl₂ was made by reacting 2.5 g 500 mesh with 37% HCl at 80°C on a hotplate in a water bath, then stirring at 200 rpm in an open state for 120 minutes. The reactions produced a clear solution (SnCl₂ solution). The white precipitate (SnCl₂ crystal) was formed slowly. The sample was cooled at room temperature then calcined using a furnace at 200°C with a heating rate of 10°C min⁻¹ for 60 minutes. Then, cooled at room temperature and crushed with a mortar to produce SnCl₂ powder. The steps were repeated for 400 mesh and 200 mesh tin particle sizes, HCl concentrations of 6, 9, 12 M, and reaction temperatures of 70°C and 90°C.

The synthesis of SnSO₄ began with mixing (NH₄)₂SO₄ with 10 ml of water using a magnetic stirrer for 10 minutes. Then produced SnSO₄ from the reaction:

\[
\text{SnCl}_2(s) + (\text{NH}_4)_2\text{SO}_4(\text{aq}) \leftrightarrow \text{SnSO}_4(s) + 2\text{NH}_4\text{Cl}(\text{aq}) \tag{1}
\]

The mass of SnCl₂ used was 5 grams. (NH₄)₂SO₄ was 3.48 grams. Furthermore, a PEG 6000 plasticizer solution was made with a mass to water ratio of 1 gr:10 ml, added to the reaction. The mixture was stirred for 1 hour without heating. Then decantation was carried out on the solution with centrifugation and washing the sample by adding 10 ml of water into the solution. Then the solution was dried in an oven at 50 degrees for 7200 minutes. The SnSO₄ obtained was analyzed using FT-IR.

3. Results and discussion

3.1 SnCl₂ synthesis

Tin from the powderization process that did not meet the industry requirements specification was used as a source of Sn in this research. Meanwhile, the source of Cl⁻ ions were taken from 37 wt% HCl, because HCl is the best source of Cl⁻ ions compared to the others [14, 15]. The chemical reaction is as follows:

\[
\text{Sn}(s) + 2\text{HCl}(l) \rightarrow \text{SnCl}_2(l) + 2\text{H}_2(g) \tag{2}
\]

\[
\text{SnCl}_2(l) + \text{heating} \rightarrow \text{SnCl}_2(cr) \tag{3}
\]
There are three variables evaluated in this study; Sn particle size, HCl concentration, and reaction temperature. The purpose of the three treatments was to determine the optimum results and conditions in the synthesis of SnCl₂, where these three would influence each other. The yield of SnCl₂ can be seen in Table 1.

| Variable | Powder Size (mesh) | HCl Concentration (M) | Reaction Temperature (°C) | Yield (%) |
|----------|--------------------|-----------------------|---------------------------|-----------|
| 1        | 200                | 12                    | 80                        | 90        |
| 2        | 400                | 12                    | 80                        | 81        |
| 3        | 500                | 12                    | 80                        | 95        |
| 4        | 500                | 6                     | 80                        | 61        |
| 5        | 500                | 9                     | 80                        | 87        |
| 6        | 500                | 12                    | 80                        | 95        |
| 7        | 500                | 12                    | 70                        | 91        |
| 8        | 500                | 12                    | 80                        | 95        |
| 9        | 500                | 12                    | 90                        | 83        |

The first treatment is the effect of Sn particle size. The sample conditions were reacted at 80°C with a concentration of 12 M HCl open reaction. The finer the Sn particle size, the easier it is to react, the greater yield was achieved. In this research, the optimum Sn particle size was 500 mesh.

The second treatment is the effect of the reaction temperature with the resulting SnCl₂ yield. Sn's particle size was 500 mesh, and the reaction temperature was 80°C open state reaction. Table 1 shows that HCl's concentration is directly proportional to the SnCl₂ produced, making more and more products. In this research, the most optimum concentration of HCl was 12 M.

The third treatment is the effect of the reaction temperature with the resulting SnCl₂ yield. The sample conditions were Sn 500 mesh, particle size 12 M HCl concentration, and open reaction. Table 1 shows that increasing the temperature tends to increase the reaction speed and produce a higher yield. However, further increasing the temperature to 90°C decreases the yield significantly. In this research, the most optimal temperature occurred when the reaction took place at 80°C, and the temperature tone of 90°C has decreased yields. It is possible because the reaction took place in an open state, while the nature of HCl is relatively volatile. In high temperatures especially, HCl evaporates more quickly into the environment, and the vapor does not react with Sn particles so that the resulting final product will also be reduced.

3.2 SnSO₄ synthesis

FT-IR characterization was carried out with samples of synthesis results and samples from calcination results, and samples from commercial SnSO₄ of PT. Timah. The results of this test are graphs between transmissions and wavenumbers. This test was carried out to determine the bonding of compounds from samples of synthesis and calcination compared with SnSO₄ from PT. Timah.
Figure 1. FT-IR Result of SnSO₄

The results of FT-IR characterization are shown in Figure 1. From Figure 1 it can be seen the spectrum comparison of the three samples. From the three SnSO₄ samples, there are spectrum characteristics of certain wavenumbers. SnSO₄ + PEG-6000 has a spectrum of (cm⁻¹) 555.78; 570.84; 599; 21; 643.39; 689.96; 966.01; 1103, 07; 1178.91; 1414.29; 1617.30; 1717; 42; 2836.48; 3061.22; and 3168.15. For commercial SnSO₄ it has a spectrum of (cm⁻¹) 634.15; 885.19; 1189.40; 1504.15; 1654.13; 1718.52; 2835.19; and 3448.10. Whereas for SnSO₄ after calcination has a spectrum of (cm⁻¹) 988.30; 1155.53; 1262.45; 1431.23; 1747.32; and 3032.26.

The characteristic spectrum of the S-O stretch [νs-o (SO₄)] is in the 900-1500 cm⁻¹ area, and the S-O deformation [δs-o (SO₄)] is in the 400-700 cm⁻¹ area [16]. For the sulfate group characteristics based on previous research, the sulfate group is in the area of ~ 1181 cm⁻¹ [17]. When viewed from the peak of characterization in commercial SnSO₄, the sulfate group area reads on a spectrum of 1189 cm⁻¹ and at SnSO₄ + PEG-6000 at the peak of 1178 cm⁻¹. As for the calcined SnSO₄, there is a weak spectrum in the area of 1155 cm⁻¹, which may be a spectrum of the sulfate group.

In SnSO₄ + PEG-6000, there is a strong spectrum at 1414 cm⁻¹, where the spectrum is the N-H spectrum [18]. The peak confirmed that the synthesized SnSO₄ before calcination still had impurities that had not been dissolved when washing the sample. The spectrum of wave numbers 1600-1700 cm⁻¹ is characteristic of OH bending [δ O-H (H₂O)], OH stretch (2800-3250 cm⁻¹ [νO-H (SOH)], and 3100-3700 cm⁻¹ [ νO-H (H₂O)]). For O-H bending spectrum regions appear in commercial SnSO₄ and SnSO₄ + PEG-6000 samples. As for SnSO₄, the results of calcination did not show any spectrum in the area. For the O-H spectrum, the νO-H (SOH) spectrum appeared in all three samples tested by the FT-IR spectrometer. As for the O-H region, the νO-H (H₂O) strains only appear in commercial SnSO₄ samples.
4. Conclusion
The synthesis of Stannous chloride (SnCl2) was successfully carried out. Based on the result of the research, the optimum conditions are as follows. The finer the particle size of tin, the higher the HCl concentration, and the higher the reaction temperature, the higher the final product. The optimal condition is when the tin powder particle size is 500 mesh with HCl 12 M at 80°C, with a percentage of 95%.

The synthesis of crystal SnSO4 with the reaction of SnCl2 tin powderization waste processing results and (NH4)2SO4 can be carried out using stirring techniques with the addition of plasticizer. The results of the FT-IR spectrometer showed a spectrum of sulfate groups in the region ~ 1181 cm⁻¹.

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