Powder Technology 311 (2017) 416–425

Contents lists available at ScienceDirect

Powder Technology

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

Synthesis of tin (II) sulfide: Determination of the reaction kinetics through calorimetric techniques

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ARTICLE INFO

Article history:
Received 27 June 2016
Received in revised form 22 August 2016
Accepted 31 January 2017
Available online 3 February 2017

Keywords:
Tin (II) sulfide synthesis
Thermal runaway
Adiabatic calorimetry
Brake pads solid lubricants

ABSTRACT

In the last ten years, the search for new application materials has become one of the "must" in the field of powder technology. Particularly, as regards solid lubricants, concerns in the use of compounds containing Lead and Antimony have been raised, since the former is classified as a carcinogen and the second such as a suspect one. Therefore, as consequence of both more and more stringent law requirements for environmental emissions and low impact on human health, safe and cheap materials are strongly demanded. As the sake of example, Tin (II) Sulfide, SnS, has been widely tested and found to be not only technically superior with respect to other alternatives but also safer from the environmental point of view. Despite these properties, its development has been limited by the relatively high synthesis costs compared to its competitors.

The aim of this work is to determine the kinetics of a safe "dry" batch process for the production of SnS using only cheap calorimetric techniques. The results obtained from this study (synthesized in a series of equations describing the dynamics of the process) have shown that a simple but complete calorimetric analysis is able to overcome the main criticality that characterizes a dry synthesis involving Sulfur and Tin: that is, the difficulty in the reactor temperature control (danger of thermal runaway) due to the extremely fast and high exothermicity of the reaction and the low thermal capacity of the reacting mixture.

1. Introduction

In recent years, Tin (II) Sulfide (SnS) has been re-evaluated as a safe and cheap material (not only as an intermediate to obtain pure Tin) to be widely used in fields such as brake pads [1] and solar cells [2].

Particularly, as regards brake pads, concerns in the use of compounds containing Lead (a carcinogen) and Antimony (a suspect carcinogen) have been raised because of the more and more stringent law requirements on powder emissions and impact on human health. Among a series of new tested materials, Tin (II) Sulfide has been found to be not only technically superior with respect to other old alternatives (note that precise details regarding the formulations of brake pads are rarely discussed in the literature because of industrial confidentiality) but also safer from the environmental point of view [3]. Despite these properties, its production, as solid lubricant in the form of finely subdivided powder, has been limited by the relatively high cost compared to its rivals and from the consecutive poor supply.

Particularly, the main criticality, which makes all the processes aimed at obtaining SnS so expensive, is the difficulty in the reactor temperature control because of the extremely high reaction rate and exothermicity together with the low heat capacities of the involved synthesis materials. In the scientific literature, there are many different production methods for Tin-Sulfur compounds; anyway they can be subdivided into two groups: "wet" and "dry" methods.

The first category deals with the reactions of solutions that lead to the precipitation of the desired product [1]. Unfortunately, such methods imply too high costs (solutions must be regenerated and exhausted materials disposed) and therefore they are not competitive as full scale processes for the production of SnS.

The second category includes all the reactions that start from reactants in the solid state. Since they are relatively cheap processes, they are the only ones which can be used for the development of an industrial synthesis on full plant scale.

As the sake of example, a dry process that leads to the formation of single SnS crystals proceeds through a direct reaction between molten metallic Tin and Sulfur at a temperature of about 400 °C, in the presence of graphite (used in order to prevent oxidation phenomena) [1]:

$$\mathrm{Sn} + \mathrm{S}(+\mathrm{C}) \rightarrow \mathrm{SnS}(+\mathrm{C}) \qquad (1)$$

In another dry process [4], the same reaction is carried out in a temperature range of 600–750 °C: however it is underlined the need to feed the reactants in stoichiometric ratio, but without the use of graphite. In

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http://dx.doi.org/10.1016/j.powtec.2017.01.096
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both these last two processes, Tin (IV) Sulfide, SnS_2, can be generated (in variable amounts) as unwanted by-product.

For all of these processes, it is important to emphasize that it has not been possible to find studies which explained in detail how the reactions occur: that is, the reaction kinetics in terms of reaction steps and related kinetic parameters. Moreover, independently on the dry synthesis path chosen for the production of such compounds, the industrial process unavoidably shows a series of problems which make difficult the complete understanding of the reaction kinetics and, consequently, the construction of a dedicated reactor: first among all, the extreme difficulty in the reactor temperature control.

The aim of this work is to characterize the reaction kinetics of a dry batch synthesis in order to develop a cheap and safe process which is really practical even at the industrial scale.

This is not a simple task because, the same raw materials, Sulfur and Tin, exhibit a number of criticalities. Sulfur is a highly flammable compound [3], therefore the entire process should be conducted in the absence of Oxygen, in order to avoid the triggering of violent reacting mixture oxidations. Tin usually consists of a mixture of Sn, SnO and SnO_2. Tin oxides in solid phase may react with the Sulfur giving, as unwanted products, sulfur oxides. In particular, Sulfur Dioxide (SO_2) is very dangerous to health and requires an abatement treatment. The reaction between Tin and Sulfur at elevated temperatures is extremely rapid and highly exothermic: these factors contribute to make difficult the temperature control because of an intrinsic inefficiency of the dedicated cooling system (no water or other fluids refrigeration can be employed for dry synthesis; there is only the possibility of heating the reactor walls using resistors and "cooling" it by switching them off). Moreover, the system is characterized by an extremely low thermal capacity: this means that little temperature fluctuations can be magnified by the exothermic reaction leading rapidly to a thermal runaway. Finally, the reaction involves multiple phases, therefore it is very difficult to build a mathematical model capable of correctly describing the system dynamics during all the phase transitions (melting, vaporization, etc.) that take place. In order to overcome all these criticalities, the kinetic model developed in this work uses a series of correlations which have been derived from the fitting of thermo-chemical data obtained through Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Accelerating Rate Calorimetry (ARC). These correlations have been found to be decisively accurate to correctly describe the thermal dynamics of the process (in terms of both phase transitions rate and reaction kinetics).

2. Materials and methods

As said before, the main aim of this work is to determine the kinetics of a suitable "dry" process for the production of SnS. The problem is how to choose the most performing dry process which is able to provide the following main characteristics: 1) use of cheap raw materials; 2) feasibility of realization at industrial scale (in terms of good reactor temperature control); and, 3) obtainment of a product as pure as possible. After a careful literature analysis, the process that seems to meet all these requirements is that one leading to the formation of single SnS crystals through the direct reaction between Tin and Sulfur, where the reactants are loaded into the reactor in quasi-stoichiometric ratio. Moreover, among reactants/additives, graphite has also been added for two main reasons: 1) avoiding side reactions between tin oxides (unavoidably present in the industrial Tin) and Sulfur [5,6]; 2) accentuating the lubricating characteristics of the product [7]. The overall reaction would take the form already reported in Eq. (1).

So that the reaction does not give SnS_2 as unwanted by-product, the correct amount of Sulfur has to be determined considering Tin as the limiting reagent (because it is the more expensive of the two reactants): in fact, it must be sufficient to completely react with Tin, but not enough to trigger the reaction of SnS_2 formation. Particular attention must be posed on the characterization of the reactants used, in order to identify any characteristics that could jeopardize the safety of the process; as the sake of example, impurities may be able to catalyze or participate to undesirable exothermic side reactions.

2.1. Materials characteristics

For all the experimental tests performed in this work, the following raw materials have been employed: Tin (Sigma-Aldrich®, powder with characteristic dimension <150 μm, purity >99.5%, presence of trace of metals in amounts <5500 ppm), Sulfur (Sigma-Aldrich®, in form of powder (or little flakes), purity >99.998%, presence of trace of metals in amounts<30 ppm), Graphite (Sigma-Aldrich®, powder with characteristic dimension <150 μm, purity >99.99%, presence of trace of metals in amounts <150 ppm), and Tin (II) Sulfide, synthesized using the following recipe: 70% Tin, 20% Sulfur and 10% Graphite.

2.2. Experimental techniques and methods

In order to determine a reliable kinetic model for the description of this process, it is necessary to perform the following steps: 1) in-depth characterization of reactants and products for what concerns the thermo-chemical point of view (that is, determining phase transitions dynamics and enthalpies); and, 2) determination of the main reaction kinetics.

Concerning the first step, both the reactants and the desired product have been characterized from the thermo-chemical viewpoint by means of Differential Scanning Calorimetry (DSC). This calorimetric technique allows for substances thermo-chemical characterization by comparing the thermal behavior of a sample with that one of a reference [8]. Particularly, the instrument is able to record the rate at which the sample develops or absorbs heat (dQ/dt) during a transformation and to generate characteristic diagrams that report the thermal power, exchanged with a resistance in order to maintain at the same temperature the sample and the reference, versus temperature (dQ/dt vs T) or time (dQ/dt vs t). Moreover, these diagrams show the number and the characteristics of all the thermal effects and the temperatures at which these effects take place. In this work, dynamic DSC tests, both in static nitrogen and air (to assess any oxidative effects due to the presence of oxygen) atmosphere, using a stainless steel crucible of 120 μL of nominal volume, resistant to medium pressures (<50 bar), have been carried out in order to individuate the occurrence of either endothermic (phase transitions, etc.) or exothermic (oxidations, decompositions, etc.) effects. It has been employed a standard method which provides a heating rate of 2, 5 and 10 °C/min in the temperature range between 30 and 280 °C. Then, thermal flux vs. temperature data corresponding to each of the detected effects have been processed in order to determine the thermo-kinetic parameters related to them.

Always concerning the first step, Thermogravimetric Analysis (TGA) tests have been carried out in order to evaluate the effect of the temperature on the volatility of the different substances involved in the process. Particularly, TGA is a technique in which the mass of a substance is monitored as a function of temperature, or time, as the sample is subjected to a fixed temperature program in a controlled atmosphere [9]. In this case, the samples have been processed in a nitrogen atmosphere using a standard heating rate equal to 10 °C/min in the temperature range 35–500 °C.

Concerning the second step, experimental tests in an Accelerating Rate Calorimeter (ARC) have been carried out in order to study the thermo-kinetic parameters of the main reaction (see Eq. (1)). ARC is an adiabatic calorimeter particularly suitable to study the thermal stability of homogeneous reacting systems [10]. In this work it has been used in the "HEAT"-"WAIT"-"SEARCH" (HWS) mode by carrying out the following dynamic standard test: the sample is warmed up (HEAT) by a radiant heater at a desired temperature (in this case 240 °C, the reason will be explained successively), then the instrument waits (WAIT) until all temperatures are stabilized, and, finally, it starts