



Synthesis of pyrophoric active ferrous sulfide with oxidation behavior under hypoxic conditions



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ABSTRACT

Ferrous sulfide produced by rust sulfuration in crude oil tank can cause accidents such as fire and explosion when exposed to air. It is quite difficult to determine the specific location of the sulfur corrosion products in crude oil tanks as well as to acquire for laboratory testing. Thus, ferrous sulfide with high spontaneous combustion activity is a good alternative for continuing the research of sulfur corrosion products. In this study, pyrophoric active ferrous sulfide sample was synthesized in laboratory. The synthetic sample was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with energy dispersive spectrometer (EDS), electron probe microanalysis (EPMA) and thermal analysis (TA), respectively. The tests indicated that the synthetic sample was amorphous flocculent agglomerate and the atomic ratio of Fe and S was 1:1 approximately, and the oxidative product was mainly Fe₂O₃. Non-isothermal calorimetric experiments were conducted with different heating rates. The reaction atmosphere was hypoxic with a 5:95% oxygen:nitrogen gas mix. Apparent activation energy was estimated based on iso-conversional methods. It would benefit for safety on petrochemical industries such as monitoring and early warning of fire and explosion of oil tanks caused by ferrous sulfide with the obtained parameters.

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1. Introduction

Rust forms on the inside-walls of crude oil tanks, transportation equipments and oil refining devices on account of metal corrosion. And at the same time a certain amount of active sulphur such as hydrogen sulfide and elemental sulfur consisted in crude oil can react with the rust. Sulfur corrosion will result in the formation of ferrous sulfide (FeS) which is a kind of dark brown powder [1,2] under anoxic condition. It is water insoluble solid and can lead to spontaneous combustion exposed to air just at normal pressure and temperature (NPT) [3,4]. When the process units are stopped for maintenance without inerting and decontamination, the air ingress will oxidize the iron sulfide to iron oxides [5]. Such self-ignition property of ferrous sulfide can cause drastic exothermic oxidation reaction and contribute to accidents of fire and explosion. It has

been proved that the formation of small quantities of pyrophoric iron sulfide is the key to self-heating process for dried sludge originated from tannery wastewater [6]. Thereafter it is necessary for a better understanding of the oxidative behavior of ferrous sulfide. It is useful not only for storage, transportation and refining of crude oil, but also for mitigation the adverse environmental and safety issues arising from above processings [7].

Thermal analysis and some characterization techniques are widely used in many research fields [8–10]. The available literature studying on the oxidation of active ferrous sulfide is scarce at present. As the active ferrous sulfide is difficult to obtain though site survey because of its self-ignition characteristic, it is infeasible to open the oil tank cap and get the sample. Most of researchers used bulk mackinawite with grinding instead of active ferrous sulfide powder for studying the process of oxidation reaction [11]. Some researchers have studied the oxidation of mackinawite under different conditions, e.g. temperature, oxygen concentration, particle size, humidity and so on [12–14]. Some other scholars focused on the investigation of the oxidation mechanism of pyrite (FeS₂) [15–18]. Self-heating and temperature-programmed experiments

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are conducted to achieve the kinetic analysis of mackinawite [19–22]. This substitution of purchased sample has two-side effects:

- (i) Bulk mackinawite sample is relatively stable to handle during experiments at NPT;
- (ii) It also contains impurities in mackinawite sample. Whether and how the impurities affect the oxidation reaction are not clear.

For gaseous and liquid reactions, a hypothesis of constant overall activation energy is necessary. But this hypothesis ignores that it involves non-stoichiometric reactants which are heterogeneous with multiple steps of varying activation energies in solid-state reactions [7]. The hypothesis will result in erroneous kinetic parameters [23,24] when employed for reactions involving solids [25].

The spontaneous combustion of sulfur-containing crude oil was caused by the sulfur corrosion product which was a mixture mainly containing FeS, but in order to reduce the unnecessary influencing factors, synthetic active FeS sample was the main object of study in our research [26]. The overall goal of our research work is to synthesize active ferrous sulfide [27,28] at NPT in laboratory by the liquid phase reaction method and to characterize the morphology and composition of the sample based on X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with energy dispersive spectrometer (EDS) [29–31] and electron probe microanalysis (EPMA). In order to characterize the oxidation reaction of the synthetic pyrophoric active samples, dynamic Differential Scanning Calorimetric (DSC) [32,33] measurement was taken for obtaining kinetic parameters [34] under hypoxic condition. The profound significant of the research is to provide the basic reference for activity inhibition of ferrous sulfide, prediction and prevention of fire or explosion accidents caused by ferrous sulfide spontaneous combustion in crude oil tanks, transportation equipments and oil refining devices.

2. Experimental

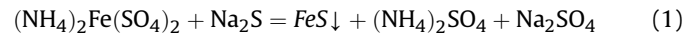
2.1. Synthesis of active ferrous sulfide

Synthesis of active ferrous sulfide sample is the first step before the thermal analysis experiments. All samples were synthesized in anaerobic environments as active ferrous sulfide is extremely sensitive to oxygen [35]. Both the synthesis and the subsequent handling of prepared iron sulfide were done inside the anaerobic chambers. The fundamental of the liquid phase reaction method [36] to produce ferrous sulfide is the reaction between ammonium ferrous sulfate solution and sodium sulfide solution. It will produce ferrous sulfide precipitation when the two solutions meet each other.

The experiment of synthesis includes two steps generally.

- (i) Put about 2 g Na₂S reagent into 10 ml deoxygenated water in a beaker to make it dissolve completely. And dissolve about 3 g (NH₄)₂Fe(SO₄)₂ reagent in another deoxygenated water at the same time.
- (ii) Add sodium sulfide solution into ammonium ferrous sulfate solution slowly with stir constantly. All the reagents were of analytical grade and used without further purification. The black suspended solid appears immediately when the two solutions meet each other. After precipitation centrifugation, abstersion with ethanol and desiccation, the high purity

active ferrous sulfide sample was obtained. The chemical reaction equation of this process can be expressed as:



The experiments of synthesized ferrous sulfide sample were repeated twice. The main reagents with mass are recorded in Table 1. A glove-box was equipped for preserving the synthetic active samples in the laboratory. Glove-box was full of inert gas such as nitrogen and filtered out the active material. It is mainly composed of a main box and a transition room. Both the water and oxygen contents are less than 1 ppm and the leakage rate is no more than 0.05 vol%/h. The samples was pumped dry in the transition room and then transferred to the main box for reserve. The structural schematic diagram of a glove-box is presented in Fig. 2. The produced sample which was synthesized based on the liquid phase reaction method has high activity of spontaneous combustion. It started to smoke in 1–2 s and appeared evident flame in 2–3 s when exposed to air at room temperature state. The burning of synthetic ferrous sulfide sample is shown in Fig. 1. This pyrophoric property of synthetic sample is very similar to the actual sulfur corrosion products in crude oil tanks just on the point that both of them will start self-heating and spontaneous combustion at NPT.

2.2. Thermal analysis test

In this study, TG-DSC instrument STA449F3 of TA Instrument was used for thermal analysis experiments as TG-DSC is a common technique in understanding the course of solid reactions [22,37–39]. During the experiment operation, approximately 20 mg of each ferrous sulfide sample is subject to temperature ramp at 0.5, 1, 2 and 4 °C/min heating rates under standard atmospheric pressure with gas flow rate of 100 ml/min. The gas consisted of 5% oxygen and 95% nitrogen because when the sample is exposed to air (21% oxygen mixed with 79% nitrogen), it is very active and the reaction of the sample would be drastic and out of control quickly. But the intensity of the reaction would be reduced under hypoxic condition (5% oxygen) [40], and the data acquisition and analysis would be easy and operable. The TG-DSC curves were measured from 25 to 400 °C.

3. Numerical tool and analysis methods

3.1. Numerical tool

An advanced thermokinetic software package was used for this study, i.e., AKTS (Advanced Kinetics and Technology Solutions) [41]. The AKTS is mainly used for calculating the apparent dynamics of aggregated solids. It is for model-free approach based on iso-conversional differential method. In AKTS software, the minimization of objective functions containing experimental and calculated values was achieved based on tangential optimization.

3.2. Flynn-Wall-Ozawa method

The oxidation of ferrous sulfide under non-isothermal condition is generally a gas-solid reaction. The kinetic equation can be expressed as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

Where α is conversion ratio, also known as reaction progress, %; T is

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