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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Oxidation of Polycrystalline Zinc Selenide with Atmospheric Oxygen

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Abstract—Oxidation of granulated polycrystalline zinc selenide (grain size 0.2-6.5 mm) with atmospheric oxygen at $430-700^{\circ}$ C was studied. The optimal conditions for the oxidation were found. An installation for the oxidation of kilogram amounts of zinc selenide was designed and fabricated.

Published data on the oxidation of zinc selenide as single crystals, polished plates, and powders include estimates of the oxidation rate at 300-950°C, composition of the reaction products, and suggested equations for the oxidation [1-5]. However, there are a number of contradictions in the determination of composition of the nonvolatile oxidation products. For instance, according to [1-3], zinc oxide is the only nonvolatile product, but in [4] significant amounts (up to 18%) of zinc selenite were found in the range 490-560°C along with zinc oxide. According to [5], zinc selenite is the main product of the oxidation at 300°C; as the temperature increases, its fraction appreciably decreases as compared to zinc oxide. Volatile oxidation products either were not investigated at all [1, 2, 5] or only their qualitative composition as a mixture of selenium and selenium dioxide [3, 4] was established. The effect of the grain size of the initial zinc selenide on the rate of its oxidation is still obscure, and probable oxidation mechanisms were not discussed.

In this work the study was concerned with waste polycrystalline zinc selenide of various grain size, formed from production of optical parts for IR technique [6]. One of the ways of processing waste products is their oxidizing calcination. In this connection, the aims of this work were to study the oxidation kinetics of granulometric zinc selenide samples of various grain size, to identify the products of the oxidation at 430–700°C, and also to study the mechanism of the oxidation with atmospheric oxygen.

EXPERIMENTAL

First we carried out a thermodynamic analysis of the system zinc selenide-air. Though the oxidation conditions were far from equilibrium, the thermodynamic analysis is important for the estimation of the relative contents of products both in gas and condensed phases. The calculation was carried out at various stoichiometric ratios of the initial reactants. The calculated equilibrium concentrations of components (in moles per total number of moles of atoms in the initial substances) for the system zinc selenide– air in excess oxidant (molar ratio zinc selenide– oxygen in the experiments was 1 : 4.5) are given in Fig. 1. Apparently, within the whole temperature



Fig. 1. Temperature dependence of the equilibrium composition of the system zinc selenide–oxygen. (*C*) Equilibrium concentration [mol (mol of atoms)⁻¹]. Phase: (a) gas and (b) condensed.



Fig. 2. Kinetic curves of zinc selenide oxidation: (α) conversion and (τ) time. Temperature (°C): (1) 700, (2) 600, (3) 550, (4) 500, and (5) 430.



Fig. 3. Variation with relative oxidation time τ/τ' of the zinc selenide conversion α . Temperature (°C): (1) 550 and (2) 700.

range (500–1500 K) the main reaction product in the gas phase is selenium dioxide. The content of the other selenium species (Se, Se₂, Se₃, etc.) is lower by several orders of magnitude. In the condensed phase selenium dioxide exists only within a narrow temperature range.

The installation for oxidation consisted of an inclined quartz reactor (30 mm in diameter and 400 mm in length) and a condenser for volatile oxidation products. When the reactor is heated in a tubular electric furnace, a steady-state convection air stream arises. The temperature in the oxidation zone was varied from 430 to 700°C during experiments. The accuracy of temperature determination did not exceed 3%. The granulometric compositions of powders were determined by sieving. The particle size of zinc selenide varied from 0.20 to 6.50 mm. Samples of powders $(18.00\pm0.01 \text{ g})$ were placed in quartz boats $(60 \times 25 \times$ 15 mm). The composition of the nonvolatile products remaining in the decomposition zone was determined by X-ray phase analysis. The qualitative composition of the volatile products condensed in the receiver was determined by chemical methods based on reactions

with sodium thiosulfate, thiourea, and a mixture of concentrated potassium iodide and hydrochloric acid [7].

We found that the main nonvolatile product in the temperature range under study is zinc oxide, with the total content of zinc selenide, selenite, and selenate being lower than 5%. The volatile product is a mixture of selenium and its dioxide. To determine the amounts of individual components, the volatile products were dissolved in distilled water, the solution was filtered, and the precipitated selenium was dried and weighed. We found that the proportion of selenium and its dioxide in volatile products varies in the course of reaction [8]. This allowed us to offer the following equation for oxidation of zinc selenide:

$$ZnSe + (0.5 + y)O_2 \longrightarrow ZnO + xSe + ySeO_2$$

In this equation factors x and y change in the course of the process, but the sum of them is equal to unity [9].

The variation of the molar ratio selenium : selenium dioxide in volatile oxidation products requires an independent study and was not considered in this work. To estimate the kinetic features, we studied only the nonvolatile oxidation products. The prevalence of zinc oxide in these products allowed us to estimate the degree of conversion of the initial zinc selenide by the gravimetric analysis. The time dependence of the zinc selenide conversion at 430–700°C is shown in Fig. 2.

To reveal the kinetic features of the oxidation, we examined the variation of the zinc selenide conversion (a) with the relative oxidation time τ/τ' (τ is current time and τ' is time of complete conversion). The dependences for 0.6-1.5-mm particles at 550 and 700°C are shown in Fig. 3. When studying the kinetics of processes in gas-solid systems, in particular of calcination of solid materials, it is common to take the model of a spherical particle with unreacted nucleus [10] as a basic model. According to this model, the limiting stage is characterized by the dependence of the conversion on the contact time, particle size, and temperature. The comparison of theoretical curves and our experimental data (Fig. 3) suggests that the oxidation process under consideration is controlled by internal diffusion [10].

The dependence of the time of 90% oxidation of zinc selenide (i.e., the reciprocal of the oxidation rate) on the particle size of the initial zinc selenide is plotted in Fig. 4. Particle sizes correspond to the mean values within the ranges (mm) 0.2-0.3, 0.3-0.4, 0.4-0.6, 0.6-1.5, 1.5-2.5, 2.5-3.5, 3.5-4.5, and 4.5-5.5.



Fig. 4. Rate of zinc selenide oxidation as a function of its particle size d: (τ_{90}) time of 90% conversion.

It is evident that the reaction rate grows considerably with decreasing particle size (the right branch of the curve), which also confirms the assumption on the internal diffusion control of the process.

At the particle size decreased further (the left branch of the curve), the oxidation rate decreases, which seems to be due to the effect of another limiting stage, namely, diffusion of oxygen through a bed of the solid product [10]. This mechanism was discussed in the literature as applied to oxidation of FeS₂ in the industrial production of sulfuric acid [11].

From our experimental data we plotted the temperature dependence of the reaction time in the coordinates $\log(1/\tau) - 1/T$ and determined the apparent activation energy of 83 kJ mol⁻¹ for the range 430– 700°C. It follows from the theory of diffusion kinetics of gas-solid phase interactions that the activation energy of processes controlled by internal diffusion is approximately a half of the activation energy of a chemical reaction [10]. The activation energy for the oxidation of polycrystalline plates of zinc selenide is known to be 170 kJ mol^{-1} [2]. In this case the activation barrier seems to be caused by the proper reaction between zinc selenide and oxygen, i.e., the reaction is kinetically controlled. The obtained apparent activation energy is approximately half of the value given in [2], which supports the assumption on the internal diffusion mode of the process.

The kinetic features allowed us to find optimal conditions for the oxidation of polycrystalline zinc selenide. This made it possible to design and fabricate an installation for the oxidation of kilogram amounts (0.6-1.5 kg) of zinc selenide [8].

CONCLUSION

Zinc oxide was found to be the main nonvolatile product of zinc selenide oxidation at 430–700°C. The oxidation is apparently controlled by internal diffusion. The temperature of 600°C and the particle size of 1.5–4.5 mm are the optimal for the oxidation of powdered polycrystalline zinc selenide by atmospheric oxygen.

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