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Effect of Mechanical Pretreatment on Thermal Decomposition of Silver Oxalate under Nonisothermal Conditions

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The effect of mechanical pretreatment on the thermal decomposition of silver oxalate was investigated using mass-spectrometric thermoanalysis. Starting at different levels of predecomposition, kinetic data were obtained by analysis of the kinetics at the initial rise of decomposition. The observed mechanically induced increase in reactivity of the silver oxalate used is due to three effects: (i) A thermally more stable "phase" at the surface of the grains is rendered ineffective by the creation of new surfaces. (ii) Disintegration processes increase the specific surface by several orders of magnitude. (iii) The number of potential nuclei in the surface is considerably increased by the generation of lattice defects.

Introduction

The kinetics of thermal decomposition of silver oxalate have been studied by a number of authors. They are essentially determined by nucleation phenomena of autolocalization character and by growth processes of the nuclei (*1*). In the investigation of these processes and of the effect of special preparation procedures (e.g., doping (*2*)) the reaction was carried out almost exclusively under isothermal conditions. In this work the effect of mechanical pretreatment on subsequent thermal decomposition is studied for a linear heating regime. Kinetic parameters were obtained using mass-spectrometric thermoanalysis (MTA) and the initial-rise method.

Experimental

The silver oxalate samples prepared according to (*3*) were relatively coarse grained. Fifty percent of their mass was made up of grains larger than 20 μm; the largest particles measured 60 μm.

Prior to thermal decomposition the samples were mechanically treated in an Ardenne-type vibrator, a mortar, or a pellet press with a pressure of 1 GPa. They weighed between 200 and 300 mg. After the mechanical treatment thermal decomposition of the silver oxalate took place in the reaction chamber of a vacuum system. In these experiments, a quantity of 5 mg was taken. The reaction gases were continuously pumped off from the reaction chamber through a constant-flow dose valve. By appropriate choice of flow the pressure in

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the reaction chamber was always kept below 100 Pa; in the initial-rise measurements, it was kept below 1 Pa. Through a second dose valve a part of the reaction gas was fed to a quadrupole mass spectrometer for analysis. The measured peak intensities for each mass were proportional to the corresponding partial pressures in the reaction chamber. The latter could be taken as a measure of the reaction rate, if the pressure changes were slow in comparison to the time constant of the vacuum system. After it had been established that CO_2 was the only gaseous reaction product from the decomposition, the intensity of the peak of mass 44 (CO_2^+) was used to measure the reaction rate. All MTA measurements were made with a constant heating rate of 1.8 K/min, while the heating rate in the initial-rise measurements was 3 K/min. With the latter method only the beginning (initial rise) of thermal decomposition was recorded, using a very sensitive setting of the mass spectrometer. These measurements were made on the same sample at different predecomposition levels indicated by the fraction of the total decomposition.

Results

Thermoanalysis of the untreated substance yielded two main peaks (Fig. 1). The low-temperature peak (LT peak) at 467 K shows a submaximum at 482 K. The high-temperature peak (HT peak) occurs at 518 K. A carbonate phase could not be detected by radiographic means at any given moment during the measurements. The amount of CO_2 set free until complete decomposition (up to 550 K) corresponded to the stoichiometric proportion of C_2O_4 in the silver oxalate. Both this result and the finding of CO_2 as the only reaction gas suggest inhomogeneities of the silver oxalate with respect to thermal stability as an explanation for the occurrence of more than one peak during thermoanalysis.

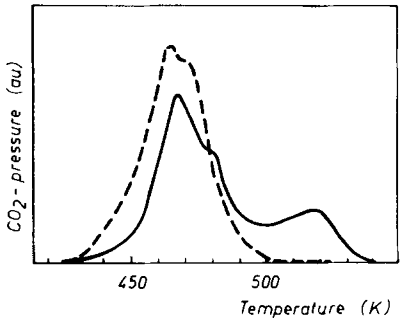

FIG. 1. MTA curves: ——, initial substance (untreated silver oxalate); ---, after 1-min mortar treatment.

When fractionating the initial substance in H_2O suspension into a fine-grained and a coarse-grained fraction, the following effects were found: For fine-grained material the submaximum of the LT peak (at 482 K) was strongly increased, while it vanished for coarse-grained material. The HT Peak was not influenced by fractionation, but it was changed markedly by treating the powder with organic solvents (acetone, methanol). It almost vanished after suspending the material in acetone, and it was reduced to about 30% after treatment with methanol. In both cases the position of the maximum of the HT peak remained unchanged, while the LT peak was shifted toward higher temperatures.

If the initial substance was mechanically treated before thermal decomposition, the HT peak vanished completely even at short activation times (1 min in an Ardenne-type vibrator). With increasing duration of treatment the LT peak lost its structure. Its maximum was shifted toward lower temperatures; after a treatment of 60 min in the Ardenne-type vibrator it was located at 450 K.

For the samples shown in Fig. 1 the decomposition kinetics under *isothermal* conditions are given in Fig. 2, where the decomposition level α is plotted vs time. The curves were obtained by measurement of the total pressure in a closed reaction

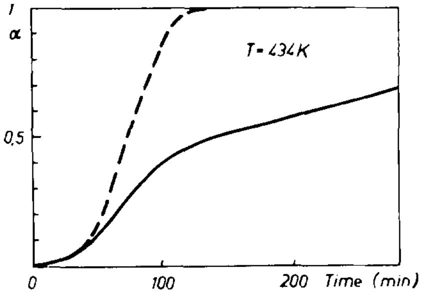

FIG. 2. Kinetics of isothermal decomposition: ——, initial substance (untreated silver oxalate); ---, after 1-min mortar treatment.

chamber. Due to the inhomogeneity of the material these curves can hardly be used for further analysis, e.g., for the derivation of kinetic parameters. As there is more than one decomposition mechanism, it makes little sense to determine a rate constant k and its temperature dependence by finding a function $g(\alpha)$ with $g(\alpha) = kt$ (*4*). This is not immediately evident, however, from the decomposition curves under isothermal conditions.

In an additional experiment the effect on the MTA curves of pelleting the material was investigated. In Fig. 3 an unpressed sample, a sample pressed at 1 GPa, and a sample pressed after mechanical treatment are compared. There are considerable changes compared to the sample which was not pressed. They can be explained essentially by two effects: First, the CO_2 diffusion is impeded by a densification of the material due to its compression. This results in a time delay with respect to measurement of the onset of decomposition. Second, as the decomposition reaction is exothermic, the higher macroscopic density leads to an inner heating of the powder. Thus the true temperature is higher than the externally measured one. For an isolated peak the resulting change in curve shape means a reduction in half-width due to the combined action of both effects. As can also be seen from Fig. 3, the HT peak cannot be eliminated by pressing alone.

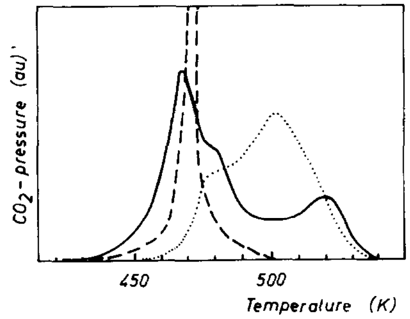

FIG. 3. MTA curves: ——, initial substance (untreated silver oxalate); · · · · ·, after pressing in a pellet press; ---, after 1-min mortar treatment and subsequent pressing.

In the determination of kinetic parameters the initial-rise method was used, as it requires the least number of assumptions with respect to a decomposition model. The only necessary condition is to assume a dependence of the type $d\alpha/dt = k \cdot f(\alpha)$ for a small interval $\Delta\alpha$ around a given level of decomposition α. Here $k = k_0 \cdot \exp(-E_A/kT)$ is a rate constant for this α. To determine activation energies a $\ln k'$ which is proportional to the decomposition rate $d\alpha/dt$ was plotted vs $1/T$. The measured curves could be well approximated by a straight line, if the following conditions held: The decomposition rate must be high enough to dominate effects of gas desorption or gas adsorption in the feed pipes of the mass spectrometer. The decomposition rate must be small enough, however, to allow the neglect of the relative change of the decomposition level $\Delta\alpha/\alpha$ within the time of measurement. This change corresponds to a change of the reactive surfaces of the nuclei. The latter condition does not hold for the onset of decomposition ($\alpha = 0$). In this case the observed activation energy E_{obsd} can be written as the sum (*5*)

$$E_{\mathrm{obsd}} = \lambda \cdot E_1 + E_g,$$

where E_g is the activation energy for nucleus generation, E_1 is the activation energy

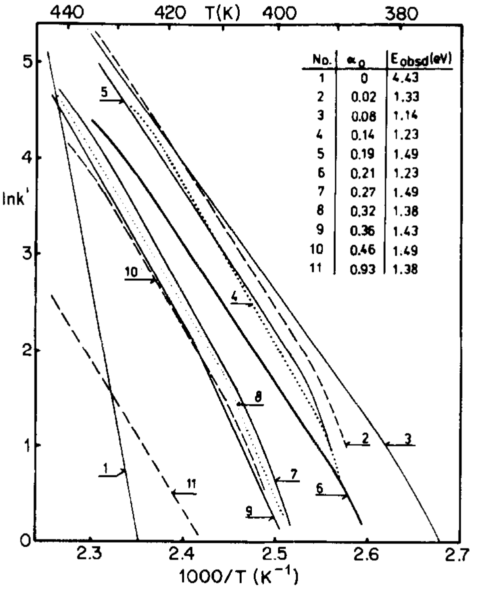

FIG. 4. Arrhenius plot of the beginning of decomposition for a mechanically untreated silver oxalate sample and for different predecomposition levels α_0. Heating for each cycle was linear in time.

for nucleus growth at the interface, and λ is a parameter depending on the geometry of nucleus growth. Figure 4 shows initial-rise measurements for the same untreated sample having gone through several heating cycles. The measured activation energies are approximately constant for $\alpha \geq 0.02$. Averaging over curves *2* to *11* gives an activation energy of 1.36 eV (131 kJ/mole). This value agrees well with published values between 105 and 151 kJ/mole. The maximum decomposition rate with respect to a given temperature was observed for $\alpha \approx 0.08$.

Figures 5 and 6 are given as examples for initial-rise measurements on mechanically treated silver oxalate samples. Treatment in the Ardenne-type vibrator leads mainly to an increase of the absolute decomposition rate for the same initial value of $\alpha (\alpha \leq 0.3)$. A change of the activation energy beyond the limits of measuring error could not be detected up to 60 min of treatment. The observed change in activation energy of curve *1* in Fig. 5 was due to illumination during storage. Exposure to light prior to decomposition results in a considerable change of decomposition kinetics, especially of nucleation processes (*6*). Here the activation energy for nucleus growth remained unchanged. The decomposition rate in the first heating cycle of a sample treated for 30 min in an Ardenne-type vibrator (Fig. 6) was found to be 2 orders of magnitude higher than that of an untreated sample at comparable temperatures. The maximum decomposition rate which occurred at about the third heating cycle was 1 order of magnitude higher than that of an untreated sample.

Discussion

There is no agreement in the literature with respect to the effect of mechanical pretreatment on the thermal decomposition of silver oxalate. The results of different au-

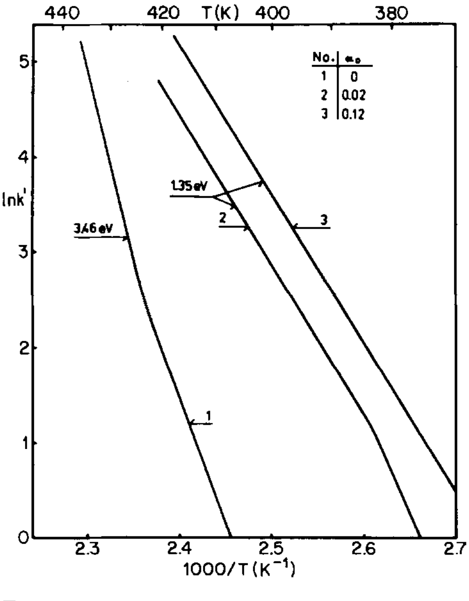

FIG. 5. Arrhenius plot of the beginning of decomposition. After a 1-min treatment in the Ardenne-type vibrator the plot was taken for different predecomposition levels α_0. Heating for each cycle was linear in time.

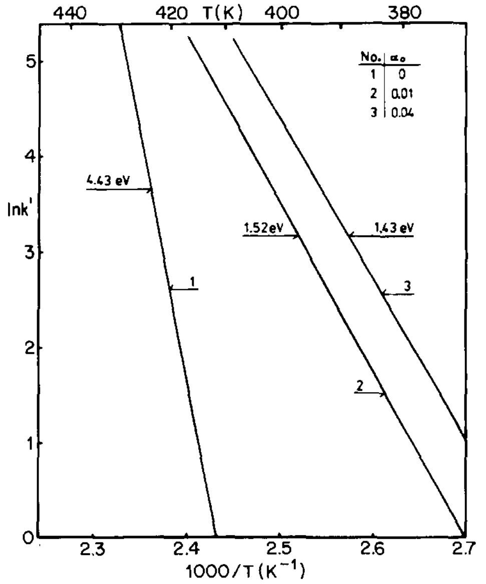

FIG. 6. Arrhenius plot of the beginning of decomposition. After a 30-min treatment in the Ardenne-type vibrator the plot was taken for different predecomposition levels α_0. Heating for each cycle was linear in time.

thors are probably dependent on preparation procedures and initial grain size of the powder used. In (*7*), for example, milling of a powder of an average grain size of 0.07 μm had no influence on the subsequent thermal decomposition. In (*8*) and other papers, however, mechanical treatment changed the kinetics of thermal decomposition. The powder used in (*8*) had an initial grain size of 8 μm. For our coarse-grained material a strong effect of treatment could thus be expected.

The processes occurring during mechanical treatment, especially decomposition effects, have been described in earlier papers (*3, 10*). No decomposition effects, however, were observed for the kind of treatment chosen for the present work.

The effect of mechanical pretreatment on thermal stability of silver oxalate can be characterized by analysis of the following parameters: homogeneity of the material, specific surface, and lattice imperfection. The initial material is inhomogeneous with respect to its thermal stability. At least two "phases" can be distinguished (LT "phase" and HT "phase"). As the initial-rise measurements yielded only one activation energy for nucleus growth for all α_0, the decomposition of the HT "phase" must proceed in a multistep process via the LT "phase":

$$(\mathrm{AgOx})_{\mathrm{HT}} \xrightarrow{k_{\mathrm{H}}} (\mathrm{AgOx})_{\mathrm{LT}} \xrightarrow{k_{\mathrm{l}}} \mathrm{Ag} + \mathrm{CO_2}.$$

Even when the activation energy of the first transformation with the reaction rate k_{H} is higher than that of the decomposition step with the reaction rate k_{l}, this will not be reflected in the initial-rise measurements. When the values of k_{H} and k_{l} have the same order of magnitude at a temperature for producing a given predecomposition level α_0, the formation of the LT "phase" of the material will always be involved. Due to its higher decomposition rate it is only the decomposition of this LT "phase" that can be recorded by initial-rise measurements. As the measurements on the effect of solvents show, the HT "phase" is situated at the surface. This "phase" which is impeding decomposition can be rendered ineffective even with little mechanical treatment due to the generation of new surfaces.

The observed fact that the HT "phase" can also be eliminated by the relatively inhomogeneous treatment in a mortar can be explained by its occurrence, particularly in coarse grains, as it is especially these grains which are affected by mortar treatment. By simple pressing, however, the HT "phase" cannot be eliminated (Fig. 3). As a possible explanation, such a HT "phase" could be formed by surface regions which contain very few potential nuclei before being mechanically treated. A relatively high density of potential nuclei on the surface of the LT "phase" is indicated by the observed fact that the decomposition rate peaks already for $\alpha \approx 0.08$. By fast coalescence of the nuclei, the maximum reactive interface and thus the maximum reaction rate are rapidly reached.

As the thermal decomposition of silver oxalate begins at the surface, the specific surface will decisively affect the reaction rate. According to (*9*) the maximum decomposition rate is (independent of the density of nuclei) inversely proportional to grain size, i.e., for constant amount of material it is proportional to the surface. Assuming a surface increase of 1 order of magnitude after a 30-min treatment, this relation is also confirmed by the measurements reported here, as can be seen by comparison of the maximum decomposition rates in Figs. 4 and 6, for example, at 400 K. A proportionality between specific surface and decomposition rate should also be expected for the beginning of decomposition, when there is no overlapping yet of the generated nuclei. A comparison of the first heating cycle in Figs. 4 and 6, however, shows that the decomposition rate of the mechanically treated sample is higher by 2 orders of magnitude than that of the untreated sample at comparable temperatures. The increased reactivity at the beginning of decomposition can be explained by two effects: First, while the microroughness of the surface cannot affect the magnitude of the maximum decomposition rate, as a surface layer of some thickness is already decomposed then, at the onset of decomposition the total surface is effective in nucleation. This microroughness, however, will not give rise to the whole enhancement at the onset. Second, mechanical treatment will increase the number of potential nuclei in the surface region. According to (*2*) this may be due to the generation of point defects, in this case Ag^+ interstitial ions. The above estimates give an increase of the defect concentration of about 1 order of magnitude as a result of mechanical treatment. These lattice defects yield an increase in the reactivity of the solid beyond the effect due to increased specific surface of treated samples.

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