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Thermal Decomposition of Yttrium-Doped Silver Carbonate

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The decomposition kinetics of yttrium-doped silver carbonate powder and pressed pellets was studied from 155° to 185°C by isothermogravimetric analysis. The extent of decomposition at constant temperature increased significantly when powdered samples were decomposed in the presence of water vapor. The decay period of the decomposition of doped silver carbonate powder obeyed a first-order rate law. The first-order rate constants can be described by the equation: $k(\sec^{-1}) = 1.52 \times 10^8 \exp(-22{,}700/RT)$. When pellets of pressed powder were decomposed, good agreement was found between the experimental decomposition rate and the rate predicted by the Polanyi-Wigner equation, thus providing evidence that yttrium-doped silver carbonate decomposes by the interface mechanism. Preirradiation (10^6 roentgens) of doped silver carbonate only slightly increased the decomposition rate.

Attention has recently focused on silver oxide because of its potential as a regenerable sorbent for carbon dioxide. Preliminary attempts have been made to promote the regeneration rate of silver oxide through the use of various dopants (*1*). Among the dopants used, yttrium appeared to be the best "catalyst" for regenerating silver oxide from silver carbonate.

Russian workers (*2*), interested in studying the influence of additives on the rate of thermal decomposition of silver carbonate, reported that cadmium increases the decomposition rate.

In this work, the effect of yttrium on the rate of thermal decomposition of silver carbonate powder and pellets was studied in further detail by isothermogravimetric analysis. The influence of water vapor, ^{60}Co γ-radiation, and temperature on the decomposition rate was examined; and a mechanism for thermal decomposition of unirradiated, yttrium-doped silver carbonate is proposed.

EXPERIMENTAL

Analytical grade silver nitrate, yttrium nitrate, and sodium carbonate were used to prepare 1 mole % yttrium carbonate-doped silver carbonate. To prepare $Ag_2CO_3 \cdot 1\%\ Y_2(CO_3)_3$, 1 liter of a 0.1 *M* solution of 99 mole % $AgNO_3$ and 1 mole % $Y(NO_3)_3$ was added slowly for 5–10 min, with rapid stirring, to 1 liter of 0.1 *M* Na_2CO_3 solution. To prepare samples containing a dopant concentration other than 1%, the same general procedure was used, but the amounts of $AgNO_3$ and $Y(NO_3)_3$ were varied. The precipitate, a light yellowish-green solid, was filtered and suspended in about 400 ml of distilled water. All subsequent treatment and storing of the precipitate was performed in photographic red light. Coleman grade carbon dioxide (stated purity, 99.99%) was bubbled slowly through the suspension for 3 hr to minimize silver oxide formation and the precipitate was collected by suction filtration on sintered glass and washed with distilled water several times. The precipitate was ground lightly and then stored over phosphorus pentoxide. Finally, the precipitate was sieved and analyzed. The $-170+250$ mesh sieve fraction was used in this work. Electron micrographs of a sample of powder from this fraction were taken and the diameters of approximately 400 particles were measured from the micrographs with the aid of a Carl Zeiss Particle Size Analyzer. The micrographs revealed that the particles were generally agglomerates of small crystallites. The mean diameter of the 400 particles (assumed to be spheres) was 8.6×10^{-6} cm and the estimated diameter of the crystallites was 2.5×10^{-6} cm. The mean diameter of the particles is smaller than expected on the basis of the mesh size because some of the agglomerates were broken up in forming the thin layer of powder necessary for taking electron micrographs.

Chemical analysis of the fraction showed 76.71 wt % silver and 0.78 wt % yttrium. On the basis of the analysis the composition of the solid was $Ag_2CO_3 \cdot 1.2\%\ Y_2(CO_3)_3$. This preparation was used in all the decomposition experiments discussed, although the conclusions reached from this preparation were confirmed with several other preparations. Debye-Scherrer X-ray powder photographs of the preparation were taken using nickel-filtered Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å).

A Cahn RH Electrobalance, enclosed in a mercury-free vacuum system, was used for the decomposition studies. Powdered samples weighing about 0.15 g (smaller samples resulted in poor contact between the sample and thermocouple for measuring sample temperature), contained in a cylindrical graphite crucible 9 mm high and of 13 mm internal diameter, were outgassed for about 1 hr (background pressure less than 10^{-3} torr) before an experiment. When required and after the outgassing, water vapor from distilled and outgassed water was admitted to the balance case from a receptacle attached to the balance hangdown tube on the tare side of the microbalance. Pressure was monitored in the balance case by means of an Alphatron pressure gage. During runs with water vapor present, the large volume of the balance case and associated components prevented the CO_2 pressure from increasing to more than 1% of the decomposition pressure for the doped carbonate at the lowest temperatures of decomposition, thus minimizing the reverse reaction. Infrared lamps for heating the sample were mounted outside the balance hangdown tube and were regulated by an electronic temperature controller. Temperature control was ±0.5°C. Sample temperature was measured with an iron-constantan thermocouple inserted in the center of the sample and supported by the balance hangdown wire. This thermocouple was calibrated by comparison with a Pt–Pt 10% Rh thermocouple and the error in calibration is estimated to be ±0.5°C. The thermocouple leads were attached to the binding posts with 0.0025-cm diameter copper wire. The maximum time for the sample to reach temperature was 2.5 min. Time zero was taken as the time heat was initially applied to the sample. Decomposition was followed by using a 1-mV Honeywell recorder and then a Honeywell 620 Digital Voltmeter coupled to a printer. The sum of the estimated weighing and recording errors is ±0.01 mg.

In addition, a series of decomposition experiments were performed on circular disks, 13 mm in diameter, which were prepared from the powder by compacting at 5700 kg/cm^2 in a laboratory press. To ensure that both sides of the pellet were exposed to the gas phase as much as possible during decomposition, the pellets were supported on 3-mm diameter spherical glass beads located in the bottom of a cylindrical graphite crucible 6 mm high and of 19-mm internal diameter.

Results and Discussion

Yttrium-doped (1 mole % as yttrium carbonate) silver carbonate was reported to exhibit an X-ray powder pattern significantly different from undoped silver carbonate (*1*). We have confirmed this finding with samples of 0.5 and 1 mole % yttrium carbonate-doped silver carbonate. Silver carbonate containing 0.1 mole % yttrium carbonate gave the same X-ray powder pattern as undoped monoclinic silver carbonate (*3*). X-Ray powder patterns, Fig. 1, clearly show the difference between the structure of 0.5% doped and undoped silver carbonate. A strong reflection at $d = 1.529$ Å (not shown in Fig. 1, but recorded on photographic film) is also characteristic

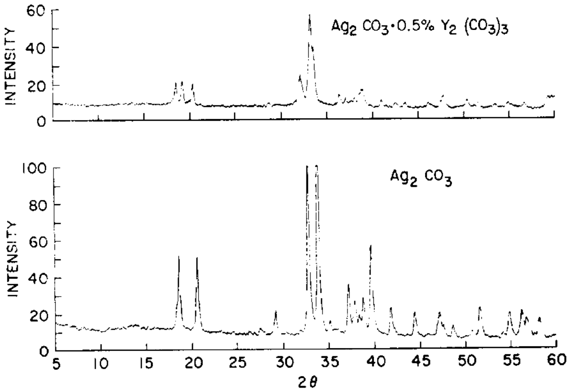

Fig. 1. X-Ray diffraction powder patterns of 0.5 mole % yttrium carbonate-doped silver carbonate and undoped silver carbonate.

of the new structure of doped samples. On the basis of the fewer reflections observed with the doped samples, it appears that the new structure is more symmetrical than monoclinic silver carbonate.

The results of experiments in which doped silver carbonate powder was isothermally decomposed *in vacuo* or under water vapor at different pressures are shown in Fig. 2. The most apparent effect of water vapor on decomposition, Fig. 2, is that the extent of reaction during the fast period of reaction increases significantly as the water vapor partial pressure increases up to about 10 torr. (Although less decomposition was found with the sample decomposed under 15 torr of water vapor than under 10 torr, this small difference is within experimental error.)

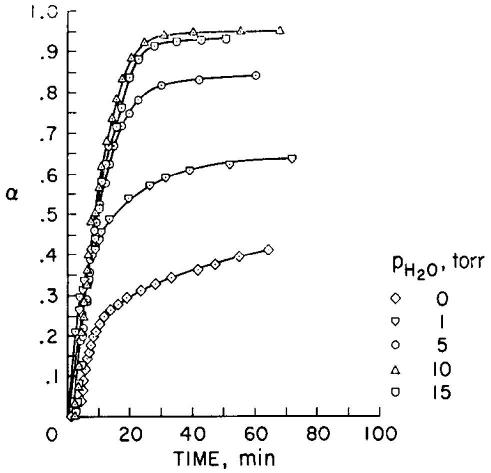

Fig. 2. Isothermal (180°C) decomposition curves for yttrium-doped (1.2 mole % as yttrium carbonate) silver carbonate powder showing the influence of water vapor on the reaction rate. For the vacuum run, the background pressure was 10^{-3} torr or less throughout the decomposition (α = moles of CO_2 lost/initial moles of CO_2 in the sample).

A possible explanation for the behavior observed with water vapor is as follows: On the assumption that yttrium-doped silver carbonate decomposes by the interface mechanism (*4*) (evidence favoring this mechanism will be presented later), it is postulated that water aids the migration of carbon dioxide through the silver oxide layer that surrounds the carbonate core. Water might assist migration of CO_2 through silver oxide by being preferentially adsorbed on oxide ion sites, thus occupying sites normally available for CO_2 adsorption. Water might also assist the migration of CO_2 through silver oxide by forming AgOH, which forms a weaker complex with CO_2 than dry Ag_2O. Furthermore, at lower water vapor partial pressures the water might not be able to penetrate the oxide layer (i.e., the rate of penetration or diffusion of water vapor is slower than the rate of decomposition); consequently, the observed rate decreases sooner than at higher water vapor pressures. The region of decomposition where the observed rate is very slow might be rate-limited by migration of CO_2 through silver oxide and not, for example, by resistance to chemical reaction.

Our findings on the influence of water vapor on the decomposition rate of yttrium-doped silver carbonate parallel those of Spencer and Topley (*5*) for undoped silver carbonate. All subsequent decomposition experiments with both powder and pellets were made in the presence of 10 torr water vapor to achieve the maximum "catalytic" influence of water.

In Fig. 3, representative isothermal decomposition curves are shown for doped silver carbonate. Although a short induction period was reported (*5*) for the decomposition of undoped silver carbonate in the presence of water vapor, Fig. 3 exhibits none for yttrium-doped silver carbonate

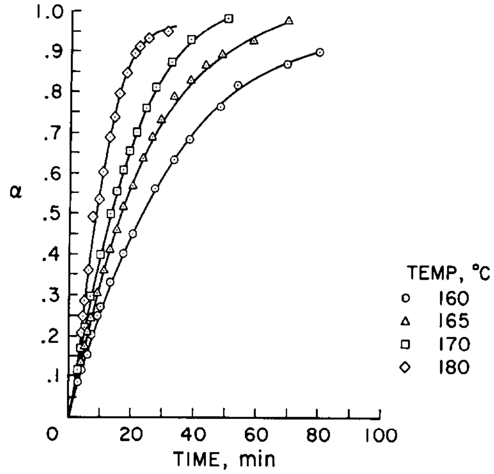

FIG. 3. Representative isothermal decomposition curves for yttrium-doped (1.2 mole % as yttrium carbonate) silver carbonate powder. Water vapor pressure was 10 torr for all runs.

over the same temperature range. A possible explanation for the absence of an induction period is that yttrium has introduced additional defects (e.g., by substitution of Y^{3+} for Ag^{1+}, thus creating cation vacancies) into the silver carbonate lattice, and these defects or high-energy sites are the origin of silver oxide nuclei.

It is also apparent from Fig. 3 that the acceleratory period is very short ($\alpha <$ 0.05) and most of the decomposition of the powder occurs during the deceleratory or decay period (from $\alpha \simeq 0.05$ to $\alpha \simeq 0.90$). A short acceleratory period can be explained if, after surface nucleation of silver oxide, the silver oxide nuclei grow rapidly, thus covering the reactant surface with a thin layer of product. No attempt was made to analyze the kinetics of the short acceleratory period. Analysis of the decomposition kinetics during the decay period showed that a first-order rate law gave the best fit to the data (see Fig. 4) over the widest range of decomposition. First-order rate constants, calculated from the slopes of lines such as those of Fig. 4, were used to construct the Arrhenius activation energy plot in Fig. 5. The activation energy for the thermal decomposition of yttrium-doped silver carbonate obtained from the slope of the latter plot is 22.7 kcal/mole with an estimated uncertainty of ±2.7 kcal/mole for a 95% confidence interval.

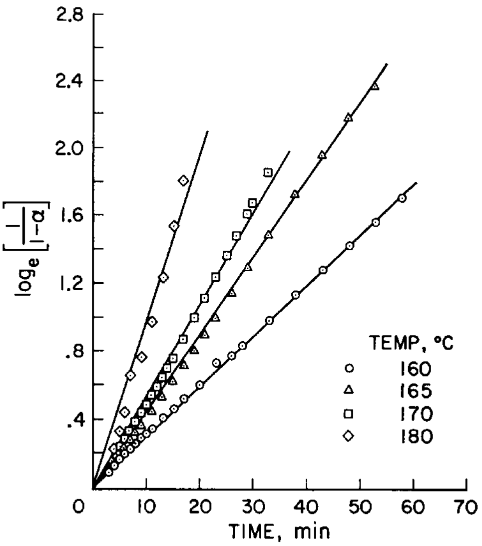

FIG. 4. Representative isothermal decomposition curves showing agreement between the first order rate law and the experimental data during the decay period for yttrium-doped (1.2 mole % as yttrium carbonate) silver carbonate powder.

The activation energy values reported for the decay period of the thermal decomposition of *undoped* silver carbonate are 22.9 and 20.0 kcal/mole (*5*, *6*). These latter values are comparable to the heat of decomposition for silver carbonate to form silver oxide and carbon dioxide, that is,

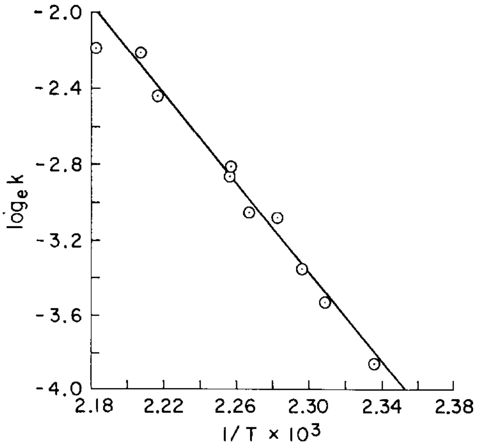

FIG. 5. Arrhenius activation energy plot from rate constants for the decay period of powdered yttrium-doped silver carbonate. Unit for k is $\min^{-1}$.

19.2 kcal/mole at 500°K (*7*). This suggested that the reverse reaction, the recombination of silver oxide and carbon dioxide, is practically without energy of activation (*6*). The activation energy for decomposing yttrium-doped silver carbonate in the presence of water is also comparable to the heat of decomposition for silver carbonate, suggesting that the rate-limiting step during the decay period is probably resistance to chemical reaction and not, for example, diffusion of carbon dioxide through the silver oxide layer. [Culbertson (*1*), using a kinetic method, has shown that the CO_2 decomposition pressures for yttrium-doped and undoped silver carbonate are comparable and, therefore, the heats of decomposition are also comparable.]

For spherical particles decomposing by the interface mechanism the rate data for the deceleratory period should obey a contracting sphere expression, $1-(1-\alpha)^{1/3} = kt$. Electron micrographs of yttrium-doped silver carbonate powder showed agglomerates of approximately circular particles, in two dimensions, with rough edges. The latter evidence prompted us to analyze our rate data for the deceleratory period by the contracting sphere expression. In doing so, we obtained less agreement between the experimental data and the contracting sphere expression than between the first order rate law and the data. This, however, does not rule out the possibility that the powder is still decomposing by the interface mechanism but instead it may suggest that the reacting surface geometry of the multilayered powder in the crucible is difficult to define.

To eliminate some of the problems associated with powders having complex interface geometry, the doped silver carbonate powder was pressed in the shape of a thin circular disk (~0.15 mm thick). The disks were then decomposed at a constant temperature on the microbalance under 10 torr of water vapor (see Fig. 6). It is apparent (Fig. 6) that the induction period is absent and the acceleratory period is very short for the disks. Reasoning similar to that used for the powder can be used for the disks to explain the absence of an induction period and a short acceleratory period.

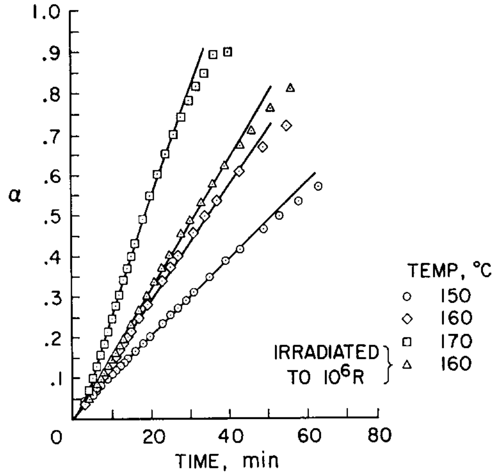

FIG. 6. Isothermal decomposition curves for pressed disks of irradiated and unirradiated yttrium-doped (1.2 mole % as yttrium carbonate) silver carbonate. Water vapor pressure was 10 torr.

If decomposition originates at the two faces of the circular disk and the oxide–carbonate interface migrates at a constant linear rate toward the center of the disk, then the following rate law should be obeyed (decomposition from the edge of the thin disk is neglected):

$$-\delta N/\delta t = kA$$

where $-\delta N/\delta t$ is the decomposition rate of doped silver carbonate in molecules/sec; k, the rate constant in molecules/sec cm^2; and A, the surface area of the two disk faces in cm^2. This equation predicts that the decomposition rate will be constant (after the oxide–carbonate interface is established) at a given temperature, since A is essentially constant for a thin disk decomposing by the interface mechanism. The decomposition data for the disks, Fig. 6, are practically linear over a wide range of decomposition, thus showing that the decomposition rate is indeed constant.

The activation energy obtained by using rate constants derived from the slopes of α versus t curves for the disks was in good agreement, 21.8 ± 4.2 kcal/mole, with that derived from the powder experiments, i.e., 22.7 kcal/mole. However, since more experiments were run with the powder, the activation energy derived from the powder data is more precise for the decomposition of yttrium-doped silver carbonate during the deceleratory period.

The Polanyi-Wigner rate expression in the following form has often been used to predict the reaction rate at an interface (*4*):

$$-\delta N/\delta t = A\tilde{N}\nu \exp(-E/RT)$$

where $\delta N/\delta t$ is the decomposition rate, molecules/sec; $\tilde{N}$, molecules of reactant per cm² of surface, molecules/cm²; A, the surface area for reaction, cm²; ν, the vibration frequency responsible for initiating decomposition, sec^{-1}; E, the activation energy for movement of the interface, cal/mole; and R,T have their usual significance.

To obtain $\tilde{N}$ for doped silver carbonate, the number of molecules of reactant per cm² of surface was assumed to be the same as for undoped silver carbonate. This assumption seems reasonable in view of the low dopant concentration. The following values were used to estimate an experimental decomposition rate for the disks by the Polanyi-Wigner equation:

$\tilde{N} = 2.33 \times 10^{14}$ molecules/cm²
$\nu = 5 \times 10^{12}$ sec^{-1} (ref. *4*)
$E = 21{,}800$ cal/mole
$T = 160°\mathrm{C}$
$A = 2.65$ cm²

The predicted rate for the disk decomposed at 160°C is 3.25×10^{16} molecules/sec and the experimental rate is 5.92×10^{16} molecules/sec. If the experimental rate agrees, within two orders of magnitude, with the rate predicted by the Polanyi-Wigner equation, then the interface mechanism is generally considered to apply (*8*). Agreement between our experimental rate for disks and the predicted rate is much better than two orders of magnitude, thus providing evidence for the interface mechanism.

If the Polanyi-Wigner equation is now used to predict a reaction rate for a powder sample the following value is obtained; 2.3×10^{21} molecules/sec using $E = 22\ 700$ cal/mole, $T = 160°\mathrm{C}$, and $A = 5.8$ m². A was estimated from the diameter of the crystallites and the sample weight, 0.14753 g. $\tilde{N}$ and ν have the same values as used for the pellets. The experimental decomposition rate determined from the slope of a straight line drawn through the powder decomposition data (from $\alpha = 0.05$ to $\alpha = 0.5$; Fig. 3), at 160°C is 9.00×10^{16} molecules/sec. Therefore, the experimental rate is approximately five orders of magnitude lower than the predicted rate when assuming the reaction is proportional to the surface area derived from the crystallite diameter. However, if the cross-sectional area of the crucible, i.e., 0.502 cm² is used for the area of the reaction interface (as opposed to the surface area derived from the crystallite size) then the predicted rate is 2.0×10^{16} molecules/sec. This value agrees well with the experimental rate.

Using the cross-sectional area of the crucible as an approximation for the area of the interface appears reasonable especially since the crystallites are very finely divided, thus permitting them to pack closely together and making it difficult for CO_2 to escape from the interior of the sample. The fact that the experimental decomposition rates for the powder samples are not much faster than for the pellets (compare Figs. 3 and 6) can also be explained if the rate for the powder is approximately proportional to the cross-sectional area of the crucible. Furthermore, it is known that crucible geometry and sample packing density can influence the way in which a powdered solid decomposes (*9*). Therefore, by choosing the appropriate area for the interface the powder decomposition data can also be explained on the basis of the interface mechanism for decomposition.

It is of interest to predict a reaction rate for the pellets which is based on the assumption that the reaction is proportional to reactant concentration (random nucleation) rather than to surface sites. From the equation reported earlier for random nucleation (*6*) and a value of 5×10^{12} sec^{-1} for the pre-exponential term, the predicted decomposition rate is 6.56×10^{23} molecules/sec at 160°C for a 100.79 mg pellet of doped silver carbonate. This value is seven orders of magnitude higher than the experimental rate of 5.92×10^{16} molecules/sec, thus providing additional indirect evidence in favor of the interface mechanism.

Garner (*4*) has tabulated a list of compounds whose decomposition kinetics have been studied, and a number of examples of endothermic decompositions are listed. In those cases when the activation energy is comparable to the heat of reaction there is generally good agreement between the rate predicted by the Polanyi-Wigner equation and the experimental rate. Agreement between the predicted and experimental rate was found in this work for yttrium-doped silver carbonate.

If either doped or undoped silver oxide is to be effective as a regenerable sorbent for carbon dioxide, it must have the desirable property of being regenerated rapidly. Russian workers (*2*) have already shown that the decomposition rate of cadmium-doped silver carbonate can be increased by preirradiation with X-rays (radiation dose, 6×10^4 roentgens). It was, therefore, of interest in our work to determine if preirradiation influenced the decomposition rate of yttrium-doped silver carbonate. Powdered samples of doped silver carbonate were preirradiated with ^{60}Co γ-radiation until the total dose received by the sample was 10^6 ($\pm 10\%$) roentgens. A disk-shaped pellet was then prepared from the preirradiated powder and decomposed at 160°C in the presence of water vapor (10 torr); see Fig. 6. It is apparent that the γ-radiation, which normally alters the electronic structure of the solid, has had only a small effect on the decomposition rate of the doped material. Several other samples of preirradiated powder that received doses of less than 10^6 roentgens were decomposed, but they showed no significant difference in decomposition rate from unirradiated samples.

Although a low concentration of yttrium has a significant influence on the crystal structure of silver carbonate, as shown by X-ray data for powders, yttrium has no apparent effect on the elementary rate-determining electronic or ionic step involved in the decomposition of silver carbonate. Yttrium impurity may, however, be responsible for the apparent absence of an induction period because it serves as a nucleation site for silver oxide. Water vapor possibly increases the decomposition rate of doped silver carbonate by aiding the migration or diffusion of carbon dioxide through the silver oxide layer. Preirradiation with γ-rays (10^6 rads) only slightly increases the decomposition rate of yttrium-doped silver carbonate. Strong evidence has been presented that favors the interface mechanism for the decomposition of yttrium-doped silver carbonate.

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