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CHARACTERIZATION OF THE GASEOUS AND
SOLID PRODUCTS OF ALUMINUM SULFATE DECOMPOSITION

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ABSTRACT

Measurements of $\text{SO}_2^+/\text{SO}_3^+$ mass spectrometer ion ratios and of weight losses when $\text{Al}_2(\text{SO}_4)_3$ is decomposed in an effusion cell show that equilibrium is achieved. Measurements of $\text{H}_2\text{O}^+/\text{SO}_3^+$ mass spectrometer ion intensities as a function of time shows that "anhydrous" aluminum sulfate contains about 0.03 moles of water per mole of sulfate ion. The solid decomposition product in the range of effusion studies, below 600°C , is an amorphous Al_2O_3 which has a surface area of $165\text{M}^2/\text{g}$ and internal pores that average about $100\text{ \AA}$ in diameter. The experimentally measured decomposition pressures are higher by more than a factor of 4 than would be expected from thermochemical calculations, probably because the heat of formation of $\text{Al}_2(\text{SO}_4)_3$ is 7 to 9 kcal per mole more positive than reported.

Key Words: Sulfur Dioxide; sulfur trioxide; aluminum sulfate decomposition; aluminum oxide, amorphous; aluminum sulfate, heat of formation, of; aluminum sulfate, water content of.

INTRODUCTION

Many metal sulfates, when heated, decompose to a solid oxide plus a mixture of SO_3 , SO_2 and O_2 gases in proportions that depend upon the temperature necessary to cause decomposition. Among reactions investigated in our laboratory in recent years were the decomposition of barium and strontium sulfates.^{1,2} These reactions yielded SO_2 and O_2 as the primary gas products in both Knudsen (equilibrium) and Langmuir (kinetic) studies. But recently, by means of a combined weight loss, torsion effusion and mass spectrometry study, Lau, Cubicciotti, and Hildenbrand³ showed that although CaSO_4 yields equilibrium SO_2 and O_2 pressures relatively readily, MgSO_4 does not. With large orifices the principal gaseous product of MgSO_4 decomposition was SO_3 . When the orifices of the cell were made sufficiently small or when Fe_2O_3 was added as a catalyst, the principal gaseous products became SO_2 and oxygen.

The temperatures suitable for effusion measurements with MgSO_4 are lower than for CaSO_4 , SrSO_4 , or BaSO_4 . It appeared of interest to investigate a sulfate decomposition that occurred at a still lower temperature to determine if under conditions for which equilibrium decomposition pressures of SO_2 , O_2 and SO_3 are calculated to be nearly equal, the equilibrium partial pressures of SO_2 can be obtained.

From available data^{4,5} it could be predicted that aluminum sulfate decomposition would be suitable for such a study. Furthermore, recent investigations by Beruto and Searcy^{6,7} of the calcium oxide produced by vacuum decomposition of CaCO_3 suggest that it should be of particular interest to investigate the crystal structure, morphology and surface area of the solid product of the reaction sequence:

Vacuum decomposition of CaCO_3 yields a CaO that is poorly crystalline, has particles with an internal porosity of more than 50%, and has surface areas of the order of $50 \text{ M}^2/\text{g}$. That oxide is much more reactive towards water vapor than is the oxide produced by decomposition of CaCO_3 in air or dry nitrogen.

The molar volume of Al_2O_3 formed from $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ can be calculated to be only 10% that of the starting material. Thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ in air at temperatures less than 275°C yields an alumina that x-ray powder diffraction studies show to be amorphous.^{4,5,6} A study by Kalinina and Pori-Koshits⁸ shows that $\text{Al}_2(\text{SO}_4)_3$ decomposes to $\gamma\text{-Al}_2\text{O}_3$ at approximately 1170°K , and then transforms to the thermodynamically more stable form $\alpha\text{-Al}_2\text{O}_3$ at temperatures greater than 1420°K . Therefore analogy with the results of CaCO_3 decomposition suggests that the alumina from $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ decomposition in vacuum might well be both metastable and highly porous. If so it might, like the oxide produced by calcite decomposition, show unusually high reactivity.

EXPERIMENTAL

The mass spectrometer used to investigate the gaseous products of $\text{Al}_2(\text{SO}_4)_3$ decomposition was 24cm. radius, Atlas CH4 magnetic deflection device equipped with a 16 stage, Cu-Be, electron multiplier for use as an ion current detector. Reagent grade $\text{Al}_2(\text{SO}_4)_3$ powder was purchased from the J. F. Baker Co. The only listed impurities were .01% Cl, .001% Fe, and .001% Pb. The powder, a hydrated form of $\text{Al}_2(\text{SO}_4)_3$, was heated for 24 hours at 620°K to drive the water off. The product then showed the expected powder x-ray pattern for anhydrous $\text{Al}_2(\text{SO}_4)_3$ (Fig. 1.).

The dried $\text{Al}_2(\text{SO}_4)_3$ was stored in a vacuum desiccator until it was transferred to a 99.5% Al_2O_3 effusion cell. The cell was heated in the mass spectrometer by radiation from a 0.025cm. diameter tungsten wire surrounded by a tantalum heat shield. Temperatures were measured with a Pt.-Pt 10% Rh thermocouple inserted in the bottom of a platinum cell holder which contained the Al_2O_3 cell.

Experiments were performed with cell lids of three different orifice diameters in order to test whether equilibrium is achieved inside the cells, and to correct for non-equilibrium if necessary.^{9,10} Orifice diameters were 0.31, 0.51, and 0.78mm respectively and the thickness of each lid was 2.31mm.

Background pressures below 10^{-7} torr were established before each run. The intensities of SO_3^+ and SO_2^+ were followed using 70 ev or 17 ev electrons. In all the decomposition runs the temperature variations were less than 2°K, and the temperatures were stable at the mid-points for long periods of time. The total fluxes of $\text{SO}_3 + (\text{SO}_2 + 1/2\text{O}_2)$ were calculated from the weight changes produced in known periods of heating. The relative amounts of SO_3 and SO_2 effused were determined by monitoring the mass 80 peak, which corresponds to $\text{S}^{34}\text{O}_3^{16}$ and both the mass 64 which corresponds to $\text{S}^{32}\text{O}_2^{16}$ and the mass 66 peak for $\text{S}^{34}\text{O}_2^{16}$.

The Al_2O_3 that formed on the decomposition of $\text{Al}_2(\text{SO}_4)_3$ was examined by the powder x-ray diffraction method and a scanning electron microscope was used to determine the characteristic particle sizes and shapes for the $\text{Al}_2(\text{SO}_4)_3$ and the Al_2O_3 product. The surface area of the Al_2O_3 and the $\text{Al}_2(\text{SO}_4)_3$ were measured using a Quantasorb Surface Area Analyzer. The samples were out-gassed for 1 to 2 hours at 625°K prior to

surface area determination to desorb water or other contaminants on the surfaces.

Pore size distributions were studied for thoroughly out-gassed samples using a high pressure (60,000 lb.) American Instrument mercury porosimeter.

RESULTS AND DISCUSSION

It has been reported¹¹ that fragmentation of SO_3 to SO_2^+ is considerable. In order to determine accurate gas composition data, the ion current ratios were measured at 17 ev (about 5 ev above appearance potentials for both ions). The effective cross section σ_{eff} for a molecule at less than maximum potential values is given by the equation

$$\sigma_{\text{eff}} = \frac{(E - \text{AP})\sigma}{(E_{\text{MAX}} - \text{AP})}$$

where AP is the appearance potential. For SO_2 , σ_{eff} is 0.52 and for SO_3 it is 0.54 based on cross sections by Mann¹² and appearance potentials determined by Lau, et al.³ When 17 volt electrons are used, fragmentation of both SO_2 and SO_3 is minimal, and the vapor effused from orifices of diameters 0.31, 0.51, and 0.78 millimeters all give $\text{SO}_2^+/\text{SO}_3^+$ ratios of 1.8/1 at 673°K. The fact that the ion ratios and calculated total pressures were independent of orifice area shows that equilibrium was attained more readily than for MgSO_4 decomposition.³ Fragmentation of SO_3 to SO_2^+ does have a significant effect when 70 volt electrons are used in studies of decomposition of $\text{Al}_2(\text{SO}_4)_3$; the $\text{SO}_2^+/\text{SO}_3^+$ ratio measured with 70 volt electrons was 2.7/1 at 673°K.

Our early $\text{SO}_2^+/\text{SO}_3^+$ ratios measured at 70 ev were higher than 2.7/1, and a scan of the mass spectrometer peaks showed the $\text{H}_2\text{O}^+/\text{SO}_2^+$ intensity ratio was approximately 1.1/1.

After some 20% of the sulfur oxide had been driven out by heating, the H_2O^+ intensity decreased to about 10 to 15% of the SO_2^+ intensity. The relative intensities then remained almost constant until the sulfate was nearly decomposed (Fig. 2).

The initial high H_2O^+ intensity probably resulted from escape of adsorbed water. When the powder was exposed to air for more than 20 minutes the ratios of SO_2^+ to SO_3^+ measured with 70 ev electrons increased to 5/1. High $\text{SO}_2^+/\text{SO}_3^+$ ratios were accompanied by high H_2O^+ intensities and a peak corresponding to H_2SO_4^+ which was about 10% of the intensity of H_2O^+ . Reaction of water with SO_3 is evidently the cause of the high $\text{SO}_2^+/\text{SO}_3^+$ ratios.

At longer times of heating, the intensities of SO_2^+ , SO_3^+ and H_2O^+ all decreased at essentially the same rate, until about 95% of the sulfur oxide content of the sample had been exhausted. The intensities then decreased at a faster rate and $\text{SO}_2^+/\text{SO}_3^+$ ratios increased as expected when insufficient $\text{Al}_2(\text{SO}_4)_3$ remains to provide the equilibrium pressures of gaseous products. The gradual decrease in ion intensities that characterized most of the period of a run is probably a consequence of poisoning of the electron multiplier by the sulfur oxides.

The fact that an H_2O^+ peak persisted at some 3% of the $\text{SO}_2^+ + \text{SO}_3^+$ intensity throughout sample decomposition appears to mean that water is a significant component of "anhydrous" aluminum sulfate, as usually prepared. This conclusion is consistent with the report by Young¹³ that he was unable to lower the water content of $\text{Al}_2(\text{SO}_4)_3$ below 0.3 wt.% of his sample, or about 2.4 mole%, of the sulfur oxide content.

Decomposition of $\text{Al}_2(\text{SO}_4)_3$ in vacuum at 720°K produced a solid product with an amorphous x-ray pattern (Fig. 3). Decomposition in vacuum at 1020°K produced a solid that showed only the three major x-ray peaks of $\gamma\text{-Al}_2\text{O}_3$ (Fig. 4). Decomposition in vacuum at 1370°K produced $\alpha\text{-Al}_2\text{O}_3$ (Fig. 5). These results are consistent with earlier results for $\text{Al}_2(\text{SO}_4)_3$ decomposition in air.⁸

The total pressures calculated from weight loss data are compared in Fig. 6 to pressures calculated from thermochemical data for $\text{Al}_2(\text{SO}_4)_3$, $\alpha\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$. Because the alumina produced in our experiments was amorphous the corresponding decomposition pressures must be lower than those when $\gamma\text{-Al}_2\text{O}_3$ is the product.¹⁴ But our measured pressures are higher than the pressure calculated for decomposition to $\gamma\text{-Al}_2\text{O}_3$ by about a factor of 4.^{5,15} Less than 10% by weight of the gaseous products was water, so loss of water does not account for the discrepancy. Furthermore, in the $\text{Al}_2(\text{SO}_4)_3$, the sulfur oxide activities should be reduced by the presence of water by an amount of the order of 3%, in accordance with Raoult's law, regardless of the form in which the water is present.

The heat of formation of $\text{Al}_2(\text{SO}_4)_3$ has been estimated to be uncertain by 5 kcal. The discrepancy between calculated and measured pressures is accounted for if it is assumed that the true heat of formation of $\text{Al}_2(\text{SO}_4)_3$ is, in fact, 5+n kcal more negative than reported, where n is the heat of formation of amorphous alumina from $\gamma\text{-Al}_2\text{O}_3$. Probably n is 1 to 3 kcal.

Scanning electron micrographs of $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ and Al_2O_3 show the hydrate and product oxide particles to be of the same shapes and dimensions, approximately 20 μm in typical cross-section. Molar volume calculations indicate that the alumina particles must have more than 85% internal porosity. The fact that the pores could not be resolved in SEM pictures

shows that either their diameters must be less than 0.1 μ m, or that reaction with water vapor during the short time of exposure to the atmosphere before SEM pictures could be made obscured the pore mouths.

Surface areas were obtained using the dynamic BET method on $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3$, and Al_2O_3 . The results are as follows:

<u>Material</u>	<u>Surface Area (M^2/gram)</u>
$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$	1.5
$\text{Al}_2(\text{SO}_4)_3$	35
Al_2O_3	165

These results coupled with the scanning electron micrographs prove that the alumina particles have very high internal surface areas.

A high pressure mercury porosimeter was used to measure the pore size distribution for the Al_2O_3 (Fig. 7). The average pore size is calculated to be 100 Å.

Because the surface area of 165 M^2/g is nearly as high as areas of catalyst supports,¹⁶ we have initiated studies to determine if the Al_2O_3 produced from $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ decomposition may be an effective reactant for removal of SO_2 and/or SO_3 from gas streams.

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FIGURES

- Fig. 1. X-ray pattern of $\text{Al}_2(\text{SO}_4)_3$.
- Fig. 2. Ion intensity vs. time at 800°K .
- Fig. 3. X-ray pattern of amorphous alumina from $\text{Al}_2(\text{SO}_4)_3$ decomposition at 720°K .
- Fig. 4. X-ray pattern of $\gamma\text{-Al}_2\text{O}_3$ from decomposition at 750°C .
- Fig. 5. X-ray pattern of $\alpha\text{-Al}_2\text{O}_3$ from decomposition at 1370°K .
- Fig. 6. Variation of equilibrium decomposition pressures with temperature. $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ vs. $1/T$. 5Kcal error bar is included on $\gamma\text{-Al}_2\text{O}_3$ line.
- Fig. 7. Pore size distribution of Al_2O_3 .

XBL776 - 5554

Fig. 1

Fig. 2

XBL776-5556

Al_2O_3
400 °C in vacuum

XBL 776-5558

Fig. 3

$\gamma\text{Al}_2\text{O}_3$
750°C in vacuum

XBL776-5559

Fig. 4

XBL776-5560

Fig. 5

Fig. 6

XBL 776-5557

XBL 776-5561

Fig. 7

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