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THE THERMAL DECOMPOSITION OF ALUMINIUM SULFATE

T. J. TRUEX, R. H. HAMMERLE AND R. A. ARMSTRONG
Ford Motor Company, Dearborn, Mich. 48121 (U.S.A.)
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ABSTRACT

The mechanism of thermal decomposition of aluminum sulfate has been investigated in the 500–700 °C temperature range using a flow reactor system with the emitted gaseous sulfur oxides collected in a Goksøyr–Ross coil and a hydrogen peroxide impinger. Sulfur trioxide (SO_3) was found to be the primary sulfur oxide released during thermal decomposition (1).

$$Al_2(SO_4)_3 \rightarrow Al_2O_3+3SO_3 \tag{1}$$

Less than 3% of the released sulfur oxides were sulfur dioxide (SO_2), indicating that the SO_3 dissociation reaction (2) is slow relative to the residence time of the SO_3 in the reactor (~1 sec).

$$SO_3 \rightleftharpoons SO_2+\tfrac{1}{2}O_2 \tag{2}$$

The experimental technique should be readily adaptable to the study of the thermal decomposition of other metal sulfates.

INTRODUCTION

A number of recent reports have dealt with the thermal decomposition of aluminium sulfate. These reports have included studies of the kinetics of decomposition[1–5] and the composition of the evolved gases formed during thermal decomposition[3–6]. The latter studies involved attempts to identify the gaseous thermal decomposition products by mass spectrum analyses and have resulted in considerable controversy concerning the identity of the primary sulfur oxide involved in the decomposition reaction. The problem in all of these studies arises from the ease of cracking of SO_3 into the SO_2^+ fragment in the ionization chamber of the mass spectrometer and therefore the difficulty of observing the SO_3 species or obtaining quantitative information on its concentration compared to other sulfur oxide species which may be present.

Recent work in this laboratory on the sulfuric acid emissions from automotive catalysts has resulted in interest in the thermal decomposition of aluminum sulfate; this interest arises from the importance of sulfur oxide storage and release reactions involving the alumina washcoat of automotive catalysts. Sulfur trioxide formed over the catalyst can react with the alumina to form aluminum sulfate at low catalyst temperatures; at higher temperatures the aluminum sulfate decomposes to release the sulfur oxides. Accordingly, the mechanism of aluminum sulfate thermal decomposition has been investigated using a flow reactor system with the emitted gaseous sulfur oxides collected in a Goksøyr–Ross coil[7] and a hydrogen peroxide impinger. The experimental method allows unambiguous determination of the concentrations of SO_3 and SO_2 formed during the dissociation reaction.

EXPERIMENTAL

The experimental apparatus used in this study is shown schematically in Fig. 1 and is essentially the same as that used to study the SO_2 oxidation kinetics over automotive catalysts[8]. Previous work has shown that this technique does not lead to spurious formation of SO_3 in the experimental apparatus[8]. A gas mixture is humidified and preheated in the first oven and then passed over a quartz boat containing aluminum sulfate in the reactor oven. As the gas leaves the reactor oven, it passes through a Goksøyr–Ross coil[7] which is maintained at 70–75 °C. This temperature is below the dew point of sulfuric acid and above that for water. Sulfuric acid selectively condenses in the Goksøyr–Ross coil while the other gases pass through. Sulfur dioxide is collected from the gas stream by oxidation to sulfate in a hydrogen peroxide impinger (3% H_2O_2) downstream of the Goksøyr–Ross coil. The amounts of SO_3 and SO_2 released during the decomposition experiments are determined by batch sulfate analyses of the Goksøyr–Ross and impinger samples, respectively. The sulfate determinations are done by barium perchlorate titration with Thorin indicator using photometric endpoint detection[9].

Baker Analyzed Reagent aluminum sulfate (dried powder) was used for all decomposition experiments. The flow reactor gas mixture was either (1) 10% H_2O and 90% N_2 or (2) 5% O_2, 10% H_2O, and 85% N_2 by volume. The presence of water in the flow reactor system is dictated by the necessity for the released SO_3 to form sulfuric acid as the gas cools upon leaving the flow

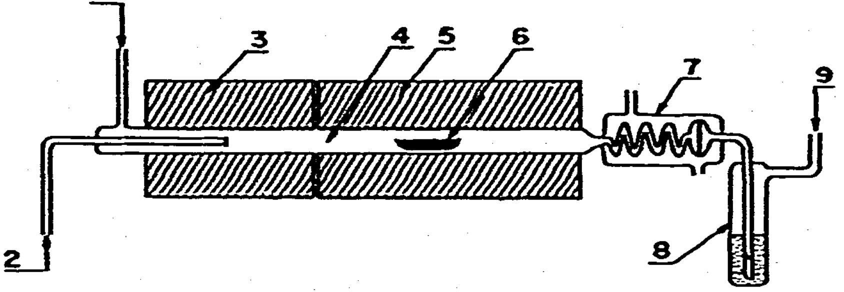

Fig. 1. Experimental apparatus. 1 = Gas inlet; 2 = water inlet; 3 = humidifier oven; 4 = quartz reaction tube; 5 = reactor oven; 6 = sample container; 7 = Goksøyr–Ross coil; 8 = H_2O_2 impinger; 9 = gas exhaust.

reactor; the Goksøyr–Ross coil will not trap SO_3 which is in the gas phase. Decomposition studies under anhydrous conditions may be performed by injecting the water downstream of the reactor zone.

The gas flow-rates for all experiments were ~5.0 l min^{-1}.

RESULTS AND DISCUSSION

The thermal decomposition of aluminum sulfate in the flow reactor in the temperature range 500–700 °C resulted in the sulfur oxide gas compositions shown in Table 1. The results in Table 1 are presented as the molar concentration ratio between the SO_3 emitted and the sum of the SO_3 and SO_2 emitted during decomposition. In the 500–700 °C temperature range, virtually all of the emitted sulfur oxide is in the form of SO_3 and thus provides conclusive evidence that this is the primary gaseous species involved in the thermal decomposition of aluminum sulfate and supports the following mechanism (1):

TABLE 1

THE RATIO OF THE MOLAR CONCENTRATIONS OF SO_3 EMITTED OVER THE SUM OF THE SO_3 AND SO_2 EMITTED (%) DURING THE THERMAL DECOMPOSITION OF ALUMINUM SULFATE

Temp. (°C)	*With oxygen*[a]	*Without oxygen*[b]
500	99%	98%
600	99%	97%
700	97%	—

[a] Gas composition 5% O_2, 10% H_2, and 85% N_2. [b] Gas composition 10% H_2O and 90% N_2.

$$Al_2(SO_4)_3 \rightleftharpoons Al_2O_3 + 3SO_3 \tag{1}$$

The very small amounts of SO_2 observed, especially the small amounts observed in the absence of oxygen, indicate that the SO_3 dissociation reaction (2) is not taking place to a significant extent in the time scale of the experiment.

$$SO_3 \rightleftharpoons SO_2 + \tfrac{1}{2}O_2 \tag{2}$$

The residence time of the SO_3 in the reactor is ~1 sec. These results indicate that the large amounts of SO_2 found in mass spectrometer studies[3–6] are either due to much longer SO_3 residence times in the reactor systems or to cracking of SO_3 in the ionization chamber of the mass spectrometer.

The experimental techniques described here are readily adaptable to the study of a wide range of metal sulfate thermal decompositions. In addition to avoiding the problem of SO_3/SO_2 measurements in mass spectrometer studies, the technique allows for decomposition studies under different gaseous atmospheres.

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