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Kinetics of the Thermal Decomposition of Nickel Sulfate

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The rate of thermal decomposition of nickel sulfate was measured in the temperature range from 1003 K to 1078 K. When a powder sample was used, this reaction was characterized as a contracting volume reaction, with apparent activation energy of 296 kJ mol^{-1}. The gaseous products were sulfur trioxide, sulfur dioxide, and oxygen. The composition of the gaseous products was near equilibrium in regard to the reaction, $SO_3=SO_2+1/2\,O_2$, because the nickel oxide formed had high catalytic activity for this reaction.

We have proposed a thermochemical hydrogen production cycle composed of the following chemical reactions (NIS process).[1]

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4 \tag{1-1}$$

$$2HI + H_2SO_4 + 2Ni = NiI_2 + NiSO_4 + 2H_2 \tag{1-2}$$

$$NiI_2 = Ni + I_2 \tag{2}$$

$$NiSO_4 = NiO + SO_3 \tag{3-1}$$

$$SO_3 = SO_2 + 1/2\,O_2 \tag{3-2}$$

$$NiO + H_2 = Ni + H_2O \tag{4}$$

Studies on the nickel salt separation[2] and dehydration equilibrium of nickel iodide[3] have been made about the process. In this paper, we report the study of reaction (3-1), the thermal decomposition of nickel sulfate.

The kinetics of the decomposition of nickel sulfate have been studied by a few investigators. Ingraham and Marier[4] measured the rates of formation and decomposition of nickel sulfate by thermogravimetry. They reported that nickel oxide was formed at a well-defined interface between sulfate and oxide, and the interface migrated into the sulfate phase at a constant rate. Also, they found that a small amount of sulfur trioxide in the decomposition atmosphere caused a substantial decrease in the rate of decomposition. The same equation was reported by other investigators,[5–7] but the apparent activation energies reported were widely different from each other as shown in Table 1. Dollimore and Pearce[8] have measured the density and the surface area of a half- hour ignition sample at various temperatures, and observed the occurrence of cracking and adhesion of particles during decomposition.

In the present work, we studied the decomposition rate, the composition of the gaseous products and the characteristics of the solid product.

Experimental

Nickel sulfate hexahydrate ($NiSO_4\cdot 6H_2O$) of analytical grade was dehydrated for 5 h at 723 K to the anhydrous form and then ground into powder.

Decomposition experiments were made with the apparatus shown in Fig. 1. The flow system was composed of a carrier gas flow controller, a vertical reactor, a sulfuric acid demister, a sulfur oxides (SO_x) trap, and oxygen meter. The reactor was made of a cylindrical quartz tube (o.d. = 15 mm) and a sintered quartz disc. The powder sample was placed on the disc and covered with quartz wool. Temperature of the reaction zone was kept constant throughout the decomposition experiment, and was measured by two alumel–chromel thermocouples. One thermocouple was put in a quartz tube inside the reactor, and the other was set at the outer wall of the reactor. Gaseous decomposition products were carried away from the reactor by argon carrier gas and the sulfur oxides were absorbed in 0.1 mol dm^{-3} iodine solution added with potassium iodide. The acid mist in the product gas stream was caught efficiently by two sintered glass filters which was moistened with the iodine solution as shown in Fig. 1.

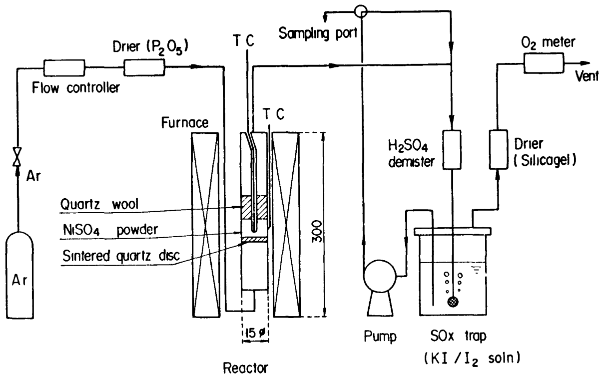

Fig. 1. Experimental apparatus (schematic).

The amounts of sulfur oxides produced were measured by acidimetry and iodometry. The oxygen concentration in the tail gas was continuously measured by an oxygen meter with zirconia solid electrolyte (Toray, Model LC 700-H).

Decomposition experiments were made with 1 g of the sample (in anhydrous form), in the temperature range from 1003 to 1078 K at 1.06×10^5 Pa pressure and 0.1 to 0.6 dm^3-NTP min^{-1} argon flow rate.

The scanning electron microscope (SEM) observation, the flowing BET surface area measurement,[9] and X-ray diffraction measurement of the sample powder were done before and after decomposition.

Results and Discussion

First, all gaseous products from decomposition were measured at all stages of the reaction. The composition of the gaseous products was found to be almost constant throughout the decomposition. Then, the fraction decomposed, α was followed by measuring the oxygen concentration. The time dependent curves of α are shown in Fig. 2 at three temperatures and an argon flow rate of 0.5 dm^3 min^{-1}. The decomposition rates decrease continuously with time. The effect of argon flow rate on the reaction rate at a constant α of 0.3, $V_{0.3}$ is shown in Fig. 3. The decomposition

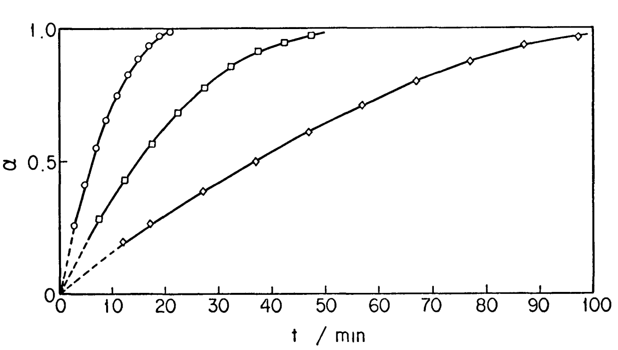

Fig. 2. Fraction decomposed (α) *vs.* time at various temperatures.
Argon flow rate: 0.5 dm^3 min^{-1}. (◇); 1023 K, (□); 1043 K, (○); 1078 K.

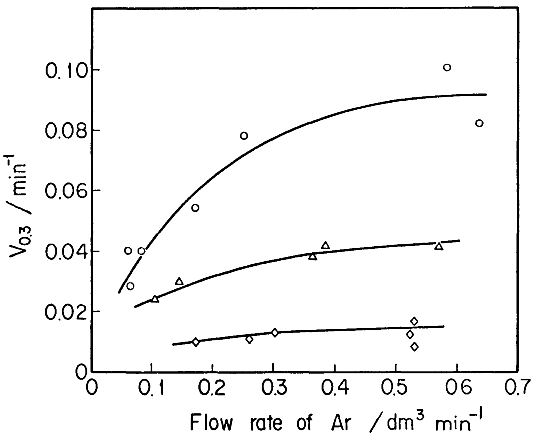

Fig. 3. Effect of argon flow rate on the decomposition rate of $NiSO_4$ when 30% of $NiSO_4$ is decomposed. (◇); 1023 K, (△); 1063 K, (○); 1078 K.

rates increase with increasing the flow rates to *ca.* 0.5 dm^3 min^{-1} and are constant above that flow rate. So, the data at a flow rate of 0.5 dm^3 min^{-1} are considered hereafter.

The rate equation of the reaction was obtained by Sharp-Brindley-Achar method.[10] By replotting α against the time normalized at $\alpha=0.5$, $t/t_{0.5}$, all data were expressed by a single curve. Then, the rate equation for the nickel sulfate decomposition could be expressed as follows:

$$1-(1-\alpha)^{1/3}=kt. \tag{5}$$

Here, k is the reaction rate constant and t is the reaction time. The plot of the experimental data according to Eq. 5 is shown in Fig. 4. A good linearity is found in the range of α to *ca.* 0.8. Equation 5 is considered for the contracting volume reaction.[11] The rate equation obtained is consistent with that previously reported.[4—7]

The Arrhenius' plot of the rate constants, k is shown in Fig. 5. From the plot, we can obtain the apparent rate parameters as follows:

$$k=1.18\times10^{11}\exp\left\{-\frac{296(\text{kJ mol}^{-1})}{RT}\right\}(\text{s}^{-1}). \tag{6}$$

Here, R is the gas constant. The apparent activation energies reported for the thermal decomposition of nickel sulfate are listed in Table 1 together with that

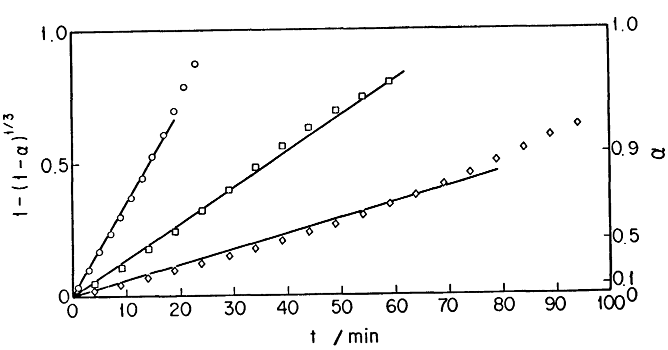

Fig. 4. $1-(1-\alpha)^{1/3}$ *vs.* time for the decomposition of $NiSO_4$.
(◇); 1023 K, (□); 1043 K, (○); 1078 K.

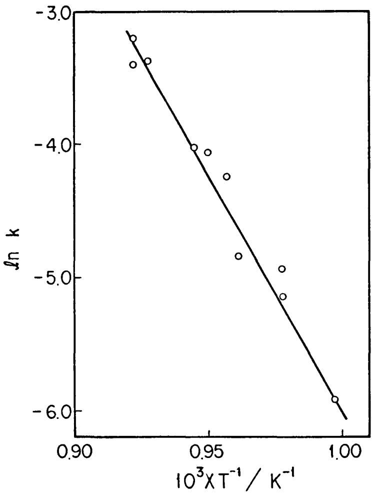

Fig. 5. Arrhenius' relationship for the decomposition of $NiSO_4$.

TABLE 1. APPARENT ACTIVATION ENERGY FOR THERMAL DECOMPOSITION OF NICKEL SULFATE

Decomposition atmosphere	Temperature range K	Activation energy kJ mol^{-1}	Reference
N_2	1031—1124	255±12	4)
Air	975—1064	115	5)
Air	1075—1250	305±32	6)
N_2 or Ar	1075—1220	162	7)
Ar	1003—1078	296	This work

obtained in the present study. Our result is close to those of Ingraham *et al.*[4] and Karwan *et al.*[6]

The X-ray diffraction pattern showed the solid product was nickel oxide, NiO. The SEM picture of the sample powder before and after decomposition are shown in Figs. 6-a and 6-b, respectively. The granular product is very porous and fluffy, and the size of product particle is much larger than that of reactant. The specific surface areas of the sample powder before and after decomposition are 8.4 m^2 g^{-1} and 15.5 m^2 g^{-1}, respectively. These observations are qualitatively explained assuming the following decomposition sequence.[8] As the decomposition proceeds, the particle is broken up into smaller particles due to the strain

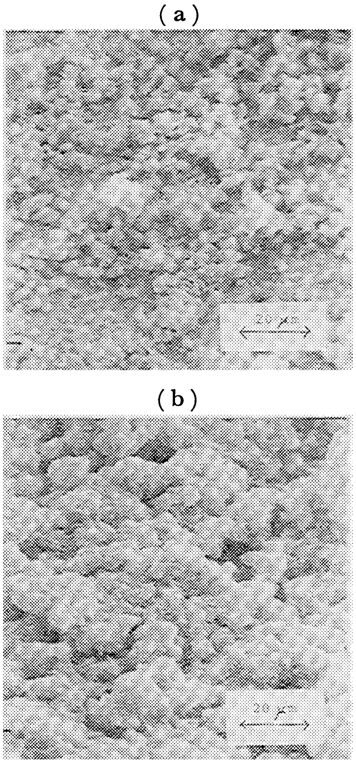

Fig. 6. (a) Scanning electron microscope picture of nickel sulfate powder used in the experiment. (b) Scanning electron microscope picture of the nickel oxide powder produced by the decomposition of sulfate at 1043 K.

imposed by the decomposition. Simultaneously, the adhesion of particles takes place and the porous and fluffy layer is formed.

The molar ratios of sulfur dioxide produced to the reactant, $NiSO_4$ at various decomposition temperatures and carrier gas flow rates are shown in Fig. 7. As seen in the figure, the ratio is almost independent of the reaction temperature and the carrier gas flow rate, and is very close to the equilibrium value which ranges from 0.88 to 0.96. The equilibrium value was calculated from the thermodynamic data[12] for the reaction:

$$SO_3 = SO_2 + 1/2\, O_2. \qquad (3\text{-}2)$$

The sulfur trioxide concentration was estimated from the amount of the reactant, $NiSO_4$ and the time difference between the time of $\alpha=0.1$ and the time of $\alpha=0.9$.

The effect of oxygen on the product gas composition was also examined using air as the carrier gas as shown in Fig. 7. At 1043 K and 0.5 $dm^3\,min^{-1}$, the ratio is 0.66. This value is equal to the equilibrium one calculated for the oxygen fraction in the carrier gas, 0.21.

These results suggest that the decomposition product, NiO acts as an active catalyst for reaction (3-2) under the experimental conditions. The catalytic activity of the nickel oxide produced was tested as follows. After the nickel sulfate was completely decomposed by heating at 1073 K for 2.5 h in an argon stream, a gas mixture of argon and 3.8 vol% sulfur trioxide was introduced to the reactor and the oxygen concentration of the tail gas was measured at 1073 K. At a contact time of 0.48 s, the fraction of sulfur trioxide decomposed was 0.77±0.07. This concentration of SO_3 and the contact time were chosen so as to simulate the thermal decomposition condition in the present study. The equilibrium fraction of sulfur trioxide decomposed under the condition is calculated to be 0.90. Thus, it was proved that nickel oxide had an enough catalytic activity for reaction (3-2) under the experimental conditions. It should be noted that the reactor wall and the sintered quartz disc had no catalytic activity for reaction (3-2). These results suggest simplification of the NIS process, because reaction (3-1) and (3-2) may be operated in one step.

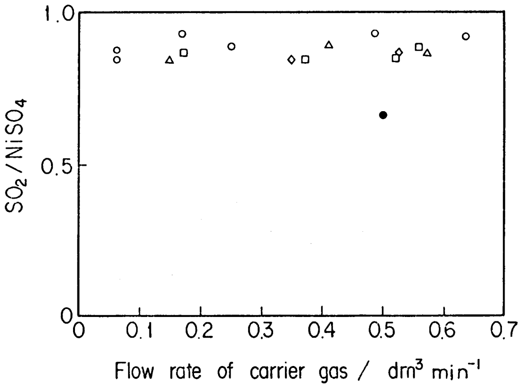

Fig. 7. Effect of the decomposition conditions on the molar ratio of SO_2 produced to $NiSO_4$.
Argon atmosphere: (◇); 1023 K, (□); 1043 K, (△); 1063 K, (○); 1078 K, air atmosphere: (●); 1043 K.

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