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NON-ISOTHERMAL STUDIES OF CERIUM(IV) OXIDE–ALKALI PERSULFATE BINARY SYSTEMS

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ABSTRACT

TG and DTA investigations, under static air atmosphere, of mixtures of CeO_2 with $Na_2S_2O_8$ and $K_2S_2O_8$ in different molar ratios (1:6, 1:3, 2:3, 1:1, and 2:1) are reported. The purpose of these investigations is to study the effect of CeO_2 on the thermal decomposition of the persulfates from ambient to 1050°C, using the derivatograph. It has been found that CeO_2 lowers the initial decomposition temperatures of these two persulfates by an amount which is directly proportional to the percentage of the oxide in the mixture through a catalytic effect. Reaction products are identified by X-ray diffraction analysis. The stoichiometric molar ratio of the solid state reaction is found to be 2 : 3 CeO_2:Na_2/K_2/S_2O_8, which leads to the formation of double salts for both persulfates, namely, $NaCe(SO_4)_2$ and $KCe(SO_4)_2$.

INTRODUCTION

The effect of some oxides on the thermal decomposition of sodium and potassium peroxodisulfates (persulfates) and the behavior of these oxides towards the thermally produced pyrosulfates have been investigated [1–3]. In addition, it has been proved that lanthanides, e.g. Gd_2O_3, Dy_2O_3 and Sc_2O_3, behave like *p*-type semiconductors [4,5].

It is also mentioned that the catalytic activity of CeO_2 lowers the decomposition temperature of hydrated lithium perchlorate [6] as follows

$$2\,LiClO_4 \cdot 3\,H_2O \underset{CeO_2}{\overset{\Delta}{\rightarrow}} Li_2O_3 + Cl_2 + 3.5\,O_2 + 6\,H_2O$$

This paper gives the results of the thermal solid state reactions of CeO_2 with sodium or potassium persulfate as well as the thermal stability of the double salts obtained, and accounts for the distinct behavior of this rare earth oxide towards either persulfate.

CeO_2 is a *p*-type semiconductor at high temperatures [7]. This property is due to its structure which has positive vacancies [8] (contains excess of Ce_{1+y}), and its

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TABLE 1

The preparation of various $CeO_2:Na_2S_2O_8$ molar ratios, and the effect of the applied heating program

$CeO_2:Na_2S_2O_8$	Sample wt. (mg)	$Na_2S_2O_8$ in sample (mg)	O_2 lost (mg)		Decompn. of $Na_2S_2O_8$ to $Na_2S_2O_7$ (°C)	
			Theor.	Pract.	T_i	T_f
0:1	200	200.00	13.40	12.50	190	225
1:6	200	178.49	11.99	12.00	180	225
1:3	200	161.16	10.83	11.00	175	220
2:3	200	134.96	9.06	9.00	160	200
1:1	200	116.08	6.56	7.00	150	190
2:1	200	81.77	5.49	6.00	190	220

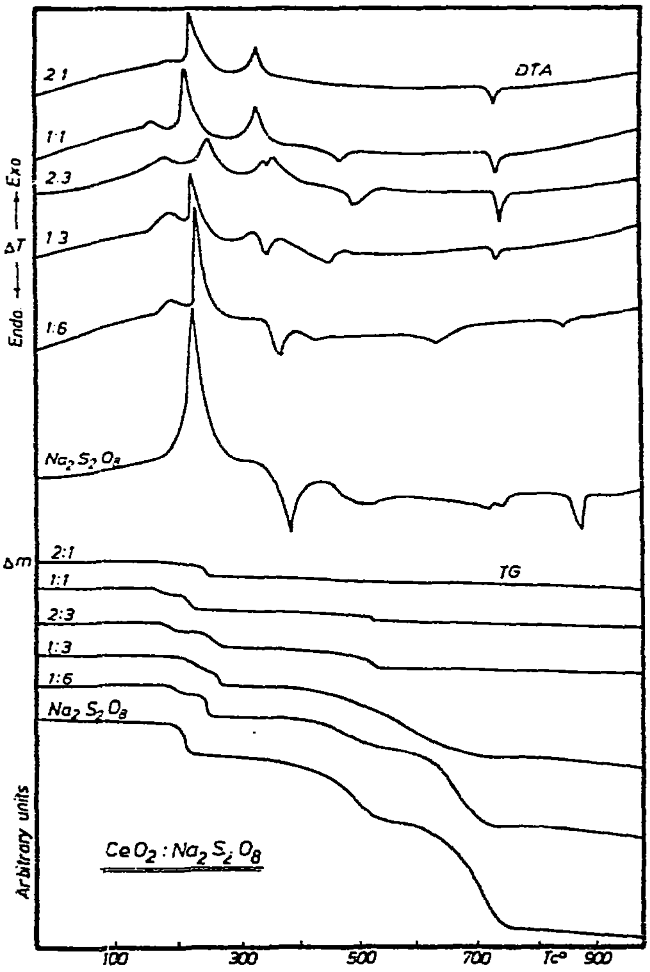

Fig. 1. TG and DTA curves of cerium(IV) oxide–sodium persulfate mixtures.

oxidation states (+3, +4). It seems that the oxide has many phases and colors due to structural changes [9]. The α-phase is CeO_2, and contains less vacancies in its crystallographic structure, while the β-phase is $CeO_{1.812}$ which is derived from eight-unit cells of the structure CeO_2, so the most stable structure of this oxide is CeO_2 which can be reduced to Ce_2O_3 at 1400°C using H_2 atmosphere.

EXPERIMENTAL

CeO_2 (> 99% pure) was supplied by Fluka AG Buches SG. All other chemicals, equipment, and techniques were as described previously [10].

RESULTS AND DISCUSSION

CeO_2–$Na_2S_2O_8$ system

Figure 1 illustrates the non-isothermal behavior of the various CeO_2:$Na_2S_2O_8$ molar ratios. The DTA curves show that the initial decomposition temperature, T_i, is lowered by an amount which is proportional to the percentage of oxide in the mixture (Tables 1 and 2). The reaction between CeO_2 and sodium pyrosulfate produced thermally, occurs after the fusion temperature of the pyrosulfate, 350–400°C, in which cerium(IV) is reduced to cerium(III). The product of the reaction is a double sulfate of chemical formula $NaCe(SO_4)_2$. This is evidenced by the XRD patterns (Table 3) of the double salt and TG curves. Calculations indicate that 2:3 CeO_2:$Na_2S_2O_8$ is the stoichiometric molar ratio which gives the stoichiometric reaction

$$2\,CeO_2 + 3\,Na_2S_2O_7 \xrightarrow{\Delta} 2\,NaCe(SO_4)_2 + 2\,Na_2SO_4 + 0.5\,O_2$$

TABLE 2

The preparation of various CeO_2:$K_2S_2O_8$ molar ratios, and the effect of the applied heating program

CeO_2:$K_2S_2O_8$	Sample wt. (mg)	$K_2S_2O_8$ in sample (mg)	O_2 lost (mg)		Decompn. of $K_2S_2O_8$ to $K_2S_2O_7$ (°C)	
			Theor.	Pract.	T_i	T_f
0:1	200	200.00	11.84	11.80	180	200
1:6	200	171.25	10.13	10.00	180	210
1:3	200	164.98	9.70	9.50	160	200
2:3	200	140.39	8.31	8.00	160	210
1:1	200	122.19	7.23	7.00	150	200
2:1	200	87.97	5.20	5.20	170	210

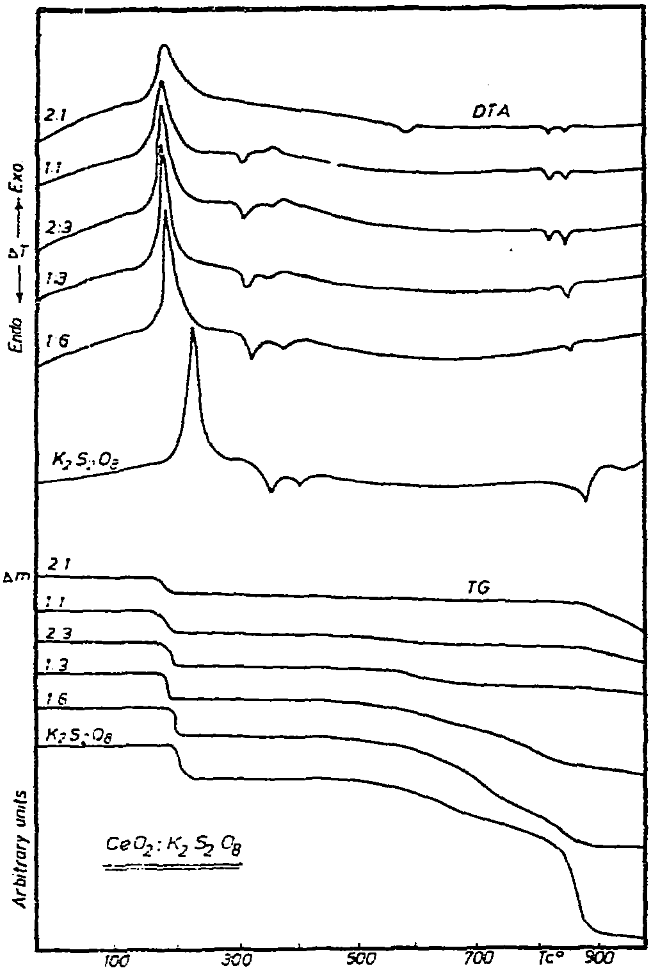

Fig. 2. TG and DTA curves of cerium(IV) oxide–potassium persulfate mixtures.

in which 78% of pyrosulfate reacted with the oxide, and this is to be considered as the optimum ratio of the reaction.

Samples sintered at 580°C gave XRD data (Table 3) identical to those available in the ASTM index cards, and belonging to the compound $NaCe(SO_4)_2$.

The horizontal plateau from 530°C to about 1050°C on the TG curve indicates the thermal stability of the product. The broad endotherm on the DTA curve, and the TG curve (weight losses of 9, 6, and 4 mg) for the 1:3, 2:3 and 1:1 molar ratios at 460–540°C indicates the decomposition of the excess pyrosulfate. The sharp endotherms at 740–775°C belong to the lowering of the melting point of Na_2SO_4 due to the presence of solid impurities of CeO_2 and $NaCe(SO_4)_2$ in various proportions.

TABLE 3

Data for XRD patterns obtained for 2:3 $CeO:Na_2S_2O_8$ system sintered at 580°C

d(Å)	2.846	3.275	4.690	4.870
I/I_0	100	78	62	57

TABLE 4

Data for XRD patterns obtained for the 2:3 $CeO_2:K_2S_2O_8$ system sintered at 840°C

d(Å)	3.118	2.720	1.904	2.164
I/I_0	100	47	26	23

CeO_2–$K_2S_2O_8$ system

Several interesting features are illustrated in Fig. 2, of which the most striking is the 2:3 $CeO_2:K_2S_2O_8$ stoichiometric molar ratio of the reaction

$$2\,CeO_2 + 3\,K_2S_2O_8 \xrightarrow{\Delta} 2\,KCe(SO_4)_2 + 2\,K_2SO_4 + 0.5\,O_2$$

which occurs at 350–400°C, i.e. directly after the β- to α-phase change of potassium pyrosulfate at 320–350°C. Calculation of the reacted percentage of pyrosulfate with the oxide is found to be 76% which is the optimum value. In the case of the 2:1 molar ratio, the DTA curve shows thermal neutrality.

The product, $KCe(SO_4)_2$, undergoes a phase change at 810°C, a fact shown on the DTA curve as an endotherm. The succeeding endotherm at 850°C refers to the melting point of the product in the presence of small amounts of K_2SO_4 and CeO_2. Samples sintered at 840°C (after the first endotherm) and at 1000°C (after the second endotherm) and identified by X-ray diffraction analysis, gave different XRD data, respectively (Table 4). However, the second sample was a melt, in the mean time the first sample did not indicate a phase change. Further, the same crystalline cubic $KCe(SO_4)_2$ was identified when samples of 1:1 molar ratio sintered at 660, 830 and 850°C, as well as samples of 1:1 ratio sintered at 760°C.

In conclusion, the thermal treatment of alkali persulfate with cerium(IV) oxide can be regarded as an alternative route for the preparation of the double salts $NaCe(SO_4)_2$ and $KCe(SO_4)_2$ by solid state reactions, other than that reported by Degtiarev et al. [11] using the reactions in solutions.

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