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THERMOKINETIC STUDIES FOR REACTIONS OF LANTHANUM(III) AND NICKEL(III) OXIDES WITH BARIUM PERCHLORATE TRIHYDRATE

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ABSTRACT

TG, DTG and DTA have been used in non-isothermal investigations of binary systems of Ni_2O_3 and La_2O_3 with barium perchlorate trihydrate, $BP \cdot 3\ H_2O$, in various molar ratios, carried out under an air (static) atmosphere from ambient to 1000°C. Ni_2O_3 catalysed the dehydration process of $BP \cdot 3\ H_2O$ and lowered its T_f by 20°C. The discontinuity on the TG curve due to an incomplete perchlorate–chlorate reaction vanished in the presence of either of the oxides: a mechanism is proposed. La_2O_3 lowered T_f by 50°C; T_i for the decomposition of BP was lowered by 150 and 100°C in the presence of La_2O_3 and Ni_2O_3, respectively. X-Ray diffractometry did not reveal any reaction between BP and the two oxides. Kinetic parameters for the decomposition steps in the presence of either of the oxides have been determined.

INTRODUCTION

Nickel(III), nickel(II) and lanthanum(III) oxides [1,2] were used for the catalytic thermal decomposition of sodium and potassium persulfates as well as for many other industrial catalytic processes. Acheson and Jacobs [3] studied the isothermal kinetics of the various decomposition steps of BP. Jasim et al. [4,5] investigated the non-isothermal kinetics of these decomposition steps in the presence of some metallic oxides using Freeman–Carroll and Coats–Redfern methods [6,7]. It was thought that the binary mixtures of either of the oxides with $BP \cdot 3\ H_2O$ should be investigated.

EXPERIMENTAL

All chemicals used were of analytical grade (puriss) from Fluka AG, Buchs SG. α-Al_2O_3 sintered at 1300°C was used as a reference material. 100 mg samples were used.

A MOM derivatograph was employed for recording the TG, DTG and DTA curves at a heating rate of $10° \min^{-1}$. A Philips X-ray diffractometer with a copper target was used to obtain the XRD patterns for the intermediate and final products of the thermal reactions.

RESULTS AND DISCUSSION

Thermal behaviour of Ni_2O_3 and La_2O_3

Figure 1 shows that Ni_2O_3 undergoes a gradual loss of oxygen (experimental, 5%; theoretical, 9.6%) which continues to the end of the heating program. In the presence of BP, its decomposition reaches a maximum

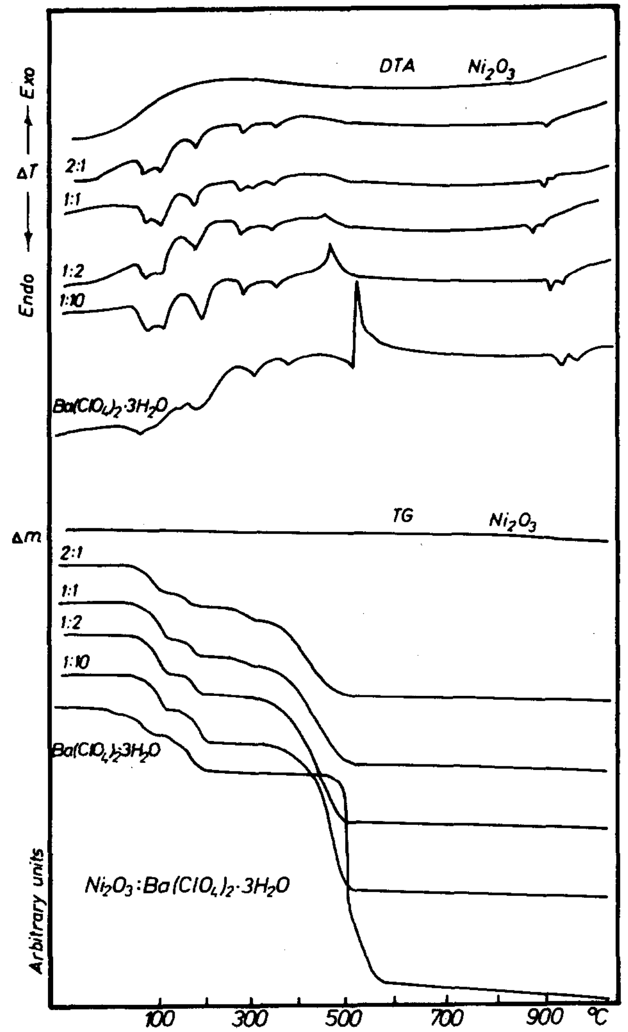

Fig. 1. TG and DTA curves for nickel(III) oxide–barium perchlorate mixtures.

between 245 and 335°C. Lanthanum(III) oxide (Fig. 3) remains thermally stable to the end of the heating program.

Ni_2O_3–BP · 3 H_2O system

Figure 1 shows the TG and DTA curves for the various molar ratios: 1 : 10, 1 : 2, 1 : 1, 2 : 1 :: Ni_2O_3 : BP · 3 H_2O. In all the ratios the T_f value for the dehydration process is lowered by 20°C due to the catalytic activity of Ni_2O_3. No change is observed in the $T_i - T_f$ interval of the phase change and decomposition of the pure BP · 3 H_2O. Also, the two (fingerprint) endotherms of $BaCl_2$ at 920 and 940°C remain as they are (Table 1), except that the small endotherm for the 1 : 2 ratio does not appear, perhaps because of the lack of sensitivity of the DTA detecting elements. X-Ray diffraction analysis confirmed the presence of $BaCl_2$ and NiO in the final products. This indicates that no reaction whatsoever takes place between the oxide and BP · 3 H_2O. It is found that the experimental loss of oxygen due to decomposition of BP, at 335–525°C, is less than the theoretical value. If the oxygen loss due to decomposition of Ni_2O_3 (245–335°C) is added to the experimental oxygen loss of BP, then the experimental and theoretical values will be the same.

The discontinuity on the TG curve of BP vanishes in the presence of Ni_2O_3; a mechanism for this is proposed. The NiO produced abstracts oxygen atoms from BP, thereby shifting the perchlorate–chlorate reversible reaction towards completion. The mechanism may be represented by the equations

$$Ni_2O_3 \xrightarrow{525^\circ C} 2\,NiO + \tfrac{1}{2}O_2$$

$$2\,NiO + \tfrac{1}{2}O_2 \xrightarrow{ClO_4^-} Ni_2O_3$$

Figure 2 shows the role of NiO as a catalyst for moving the decomposition of BP to completion, where the dissociation of Ni_2O_3 starts ahead of that of BP.

TABLE 1

The effect of Ni_2O_3 and NiO on the thermal decomposition of BP · 3 H_2O

Molar ratio, oxide : BP	Weight (%)		Phase change (BP)		Decompn. (BP)		$BaCl_2$	
	Ni_2O_3	BP · 3 H_2O	T_i	T_2	T_i	T_f	T_i	T_f
2 : 1	45.88	54.12	280	355	355	525	920	
1 : 1	39.76	70.23	280	355	340	525	920	930
1 : 2	17.51	82.49	280	355	345	525	920	940
1 : 10	4.10	95.93	280	350	345	525	920	940
	NiO	BP · 3 H_2O						
6 : 1	50	50	280	350	340	525	920	940

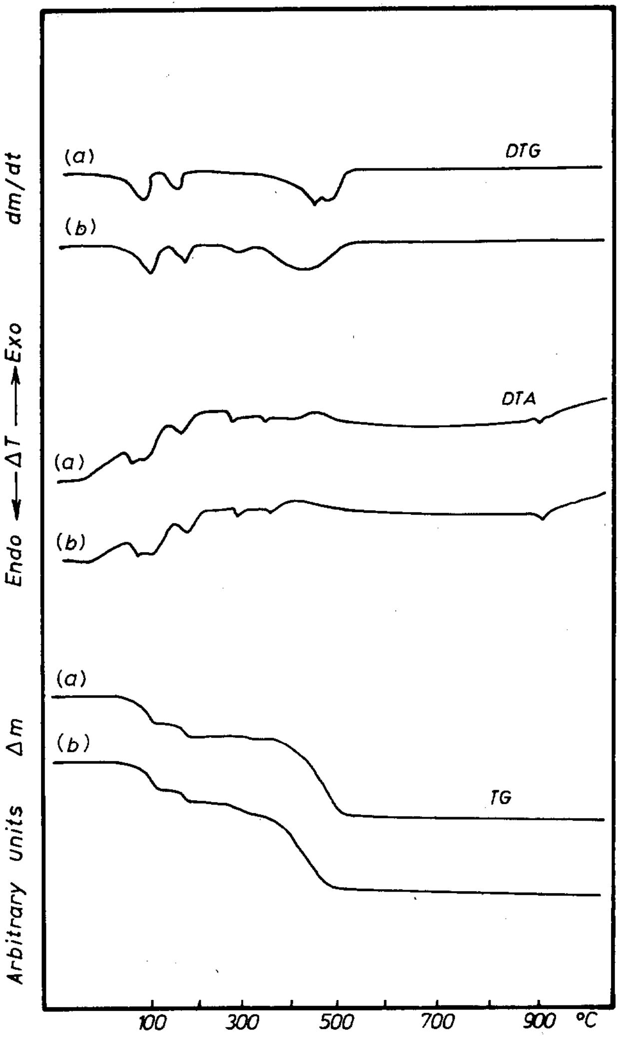

Fig. 2. TG, DTA and DTG curves for (a) 6:1 NiO–$Ba(ClO_4)_2 \cdot 3\ H_2O$ and (b) 2:1 Ni_2O_2–$Ba(ClO_4)_2 \cdot 3\ H_2O$.

La_2O_3–BP · 3 H_2O system

Figure 3 shows the TG and DTA curves for the molar ratios: 1 : 20, 1 : 10, 1 : 2, 1 : 1, 2 : 1 :: La_2O_3 : BP · 3 H_2O. Careful scrutiny of the TG curve for the 2 : 1 ratio indicates that the oxide has lowered the T_f value for the dehydration process by 70°C owing to its catalytic effect. The catalytic effect was found to increase with increasing amounts of La_2O_3, as shown in Table 2.

The oxide raised the temperature of the first phase change (α–β) from 280 to 290°C; the endotherm at 350°C due to the second phase change (β–γ) disappeared. The results in Table 2 show that the T_i value for the BP

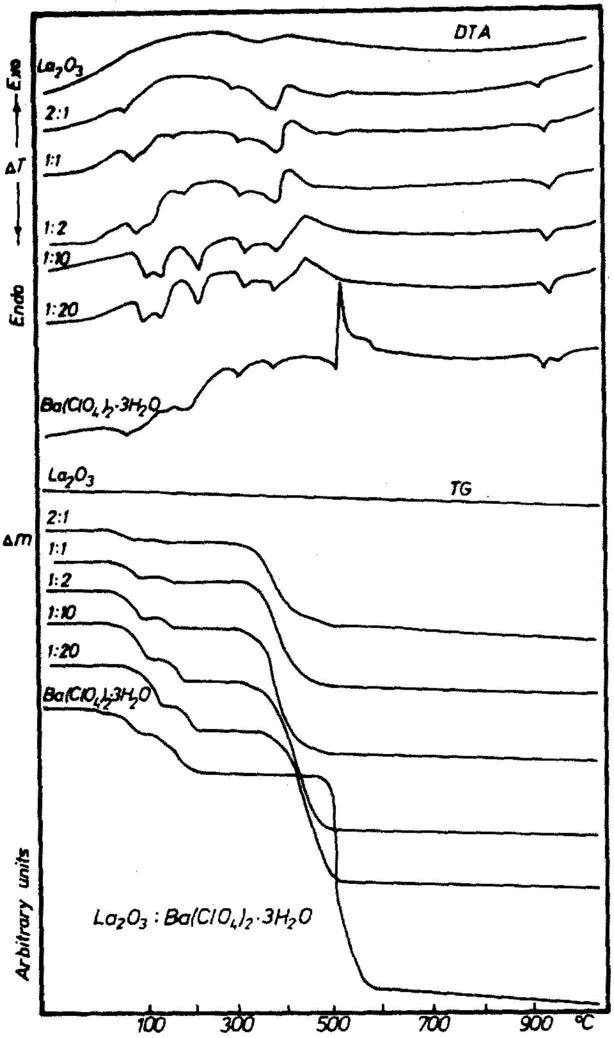

Fig. 3. TG and DTA curves for lanthanum(III) oxide–barium perchlorate mixtures.

TABLE 2

The effect of La_2O_3 on the thermal decomposition of BP·3 H_2O

Molar ratio, oxide : BP	Weight (%)		Dehydration of BP·3 H_2O T_f	Decomp. of BP		$BaCl_2$, m.pt. (°C)
	La_2O_3	BP		T_i	T_f	
2 : 1	62.59	37.41	150	300	512	
					510	920
1 : 1	45.50	54.50	160	300	510	920
1 : 2	29.41	70.59	170	300	500	920
1 : 10	7.70	92.30	190	300	500	920
1 : 20	4.00	96.00	195	320	510	920

decomposition is drastically lowered to 300°C for the 2:1 ratio, and to 320°C for the 1:20. Meanwhile the T_f value for BP becomes 510°C, owing to the catalytic adsorption of ClO_4^- ions on the surface of the oxide leading to loss of oxygen by directing the decomposition to completion, thus obviating the discontinuity.

It is to be noted that the melting endotherm of $BaCl_2$ has vanished with only its phase change at 920°C remaining, but with a larger area than usual. It looks as if the two endotherms were united due to lowering of the melting point of the chloride, which was caused by the presence of impurities, perhaps occluded in the oxide.

The large endotherm appearing at the beginning of the BP decomposition is actually the sum of the endothermic changes

$$\beta\text{-Ba}(ClO_4)_2 \xrightarrow{350°C} \gamma\text{-Ba}(ClO_4)_2 \xrightarrow{\Delta} \gamma\text{-Ba}(ClO_3) + O_2$$

$$Ba(ClO_3)_2 \xrightarrow{\Delta} Ba(ClO_2)_2 + O_2$$

Afterwards, both the TG and DTG curves assume horizontal plateaus which means that no reaction occurs from there onward. XRD patterns for samples prehated at temperatures higher than 600°C indicate the presence of $BaCl_2$ and La_2O_3 only.

Thermokinetic studies

The non-isothermal investigations carried out by us involved the estimation of kinetic parameters (order of decomposition reactions, n, activation energy, E_a, and exponential factor, log Z) from the TG and DTG curves of BP in the presence of the two promotors, Ni_2O_3 and La_2O_3, using Coats–Redfern [6] and Freeman–Carroll [7] methods. The results are summarised in Table 3, which also shows that the E_a value for the decomposition of BP has been reduced by 2.5 and 20°C in the presence of Ni_2O_3 and La_2O_3, respectively.

TABLE 3

Kinetic parameters of the thermal decomposition of BP in the presence of Ni_2O_3 and La_2O_3

Kinetic parameters	2:1 :: Ni_2O_3:BP·3 H_2O		1:1 :: La_2O_3:BP·3 H_2O	
	F–C [a]	C–R [b]	F–C [a]	C–R [b]
E_a (kJ $mole^{-1}$)	101.0	99.4	138.7	122.8
log Z	2.23	2.82	4.14	4.86
n	1.22	1.00	1.26	1.00

[a] Freeman–Carroll method, ref. 7.

[b] Coats–Redfern method, ref. 6.

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