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Thermochimica Acta 261 (1995) 119–124

thermochimica
acta

Catalytic and inhibiting effects of barium peroxide and hydroxide on the decomposition of sodium chlorate

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Received 2 November 1994; accepted 19 February 1995

Abstract

The thermal decomposition of sodium chlorate catalyzed by manganese(IV) oxide, nickel(II) oxide and copper(II) oxide in the presence of barium peroxide or hydroxide has been studied by thermogravimetric and differential thermal analysis. Barium peroxide and hydroxide are moderately active catalysts when used alone, but both become inhibitors for the decomposition of sodium chlorate catalyzed by manganese(IV) oxide, nickel(II) oxide and copper(II) oxide. The inhibiting mechanism is discussed.

Keywords: Barium peroxide; Decomposition; Hydroxide; Sodium chlorate; Transition metal oxide

1. Introduction

Sodium chlorate is used as a chemical oxygen source in chemical oxygen generators. A transition metal oxide, such as cobalt oxide or manganese dioxide, is usually used as a catalyst to facilitate the decomposition [1, 2]. Barium peroxide is used in the mixture to suppress the formation of the chlorine gas formed through side reactions and to stabilize the oxygen evolution.

The thermal decomposition of sodium chlorate catalyzed by transition metal oxides has been studied by a number of investigators [3–5], but little has been reported on the decomposition of sodium chlorate in the presence of both a transition metal oxide and barium peroxide or hydroxide. Our previous study has indicated that both barium peroxide and hydroxide have an unexpected property, which is a strong interaction

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with cobalt oxide [6]. When used alone, barium peroxide or barium hydroxide catalyzes the decomposition of sodium chlorate. When used in combination with cobalt oxide, however, they become inhibitors.

It is the purpose of this study to examine the interaction of barium peroxide and hydroxide with manganese oxide, nickel oxide and copper oxide, and to see whether the catalytic activity of manganese(IV) oxide, nickel(II) oxide and copper(II) oxide can be modified by the presence of barium peroxide or hydroxide.

2. Experimental methods

Copper oxide and manganese dioxide were prepared by decomposing the corresponding carbonates at 260 and 450°C respectively. Nickel oxide was prepared by decomposing nickel carbonate hydroxide ($\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) at 450°C. Sodium chlorate and barium hydroxide hydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$) were in the form of coarse crystalline particles, and barium peroxide was in the form of fine powder as purchased from Aldrich Chemical.

The oxide products were analyzed by X-ray diffraction analysis using a Rigaku D/maxII diffractometer. Surface areas of the metal oxides and barium peroxide were measured using a BET Sorptometer. The sample was heated at 150°C for 30 min in vacuum to drive off any adsorbed moisture and other gases prior to the measurements.

Chemical mixtures were made based on mass percentages. Each chemical mixture for thermal analysis was intimately mixed for about five minutes using an agate pestle and mortar. The total mass of each mixture was approximately 2 g. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out using a Netzsch thermal analyzer Model STA 409. The sample was heated in the furnace at 20°C min⁻¹ in an oxygen stream of 150 ml min⁻¹. The TG and DTA data were recorded simultaneously. The sample mass was approximately 100 mg.

3. Results and discussion

The manganese oxide, nickel oxide and copper oxide prepared were identified by X-ray diffraction analysis as MnO_2 , NiO and CuO respectively. The BET surface areas of the MnO_2 , NiO, CuO and BaO_2 were 58, 62, 63 and 1.0 m² g⁻¹ respectively.

The thermogravimetric analysis results of the samples of sodium chlorate with 4% manganese(IV) oxide, nickel(II) oxide and copper(II) oxide and with 0–8% barium peroxide or hydroxide are summarized in Table 1. Because the onset decomposition temperature depends on particle size and is difficult to determine unambiguously, the temperature at which 50% of the sodium chlorate has decomposed is used to compare the relative activity and is referred to as 50% DT. The 50% DTs of NaClO_3 with barium peroxide and hydroxide as previously reported [6] are given in the table as a comparison.

Manganese(IV) oxide, nickel oxide and copper oxide are all active catalysts for the decomposition of sodium chlorate as shown in Table 1. A loading of 4% of these oxides

Table 1
Decomposition temperatures of NaClO_3 with additives

Composition	50% DT/(°C)
NaClO_3	560
$\text{NaClO}_3 + 2\% \text{BaO}_2$	510 [6]
$\text{NaClO}_3 + 2\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	510 [6]
$\text{NaClO}_3 + 4\% \text{MnO}_2$	300
$\text{NaClO}_3 + 4\% \text{MnO}_2 + 2\% \text{BaO}_2$	392
$\text{NaClO}_3 + 4\% \text{MnO}_2 + 8\% \text{BaO}_2$	443
$\text{NaClO}_3 + 4\% \text{MnO}_2 + 2\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	395
$\text{NaClO}_3 + 4\% \text{MnO}_2 + 8\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	461
$\text{NaClO}_3 + 4\% \text{NiO}$	321
$\text{NaClO}_3 + 4\% \text{NiO} + 2\% \text{BaO}_2$	351
$\text{NaClO}_3 + 4\% \text{NiO} + 8\% \text{BaO}_2$	353
$\text{NaClO}_3 + 4\% \text{NiO} + 2\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	360
$\text{NaClO}_3 + 4\% \text{NiO} + 8\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	372
$\text{NaClO}_3 + 4\% \text{CuO}$	300
$\text{NaClO}_3 + 4\% \text{CuO} + 2\% \text{BaO}_2$	362
$\text{NaClO}_3 + 4\% \text{CuO} + 8\% \text{BaO}_2$	369
$\text{NaClO}_3 + 4\% \text{CuO} + 2\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	369
$\text{NaClO}_3 + 4\% \text{CuO} + 8\% \text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$	376

can lower the decomposition temperature of sodium chlorate by more than 200°C as measured by 50% DT. Barium peroxide and hydroxide also catalyze the decomposition of sodium chlorate. When they are mixed with sodium chlorate together with transition metal oxides, however, they become inhibitors and partially suppress the catalytic activity of the metal oxides. Therefore, the 50% DTs of the samples of sodium chlorate with both the transition metal oxide and barium peroxide or hydroxide are lower than those of the samples of sodium chlorate catalyzed by the transition metal oxides in the absence of barium peroxide or hydroxide.

The inhibiting effect appears to saturate at 2% loading of barium peroxide or hydroxide for the samples of NaClO_3 with 4% NiO or CuO, but increases with increased loading of the peroxide or hydroxide for the sample of sodium chlorate catalyzed by manganese dioxide. This is probably due to the oxidation of the manganese dioxide to permanganate. Permanganate has much lower catalytic activity for the decomposition of sodium chlorate [8]. It is known that in the presence of alkali metal hydroxide and a strong oxidizing agent, MnO_2 can be oxidized to manganate MnO_4^{2-} and the latter disproportionates to form permanganate MnO_4^- [9]. Barium hydroxide is chemically very similar to alkali metal hydroxide, and sodium chlorate is a strong oxidizing agent. Therefore, MnO_2 can be oxidized to the permanganate and thus have lower activity. The oxidizing ability of the permanganate decreases with increasing alkalinity of the medium. In other words, it is easier to oxidize manganese(IV) oxide to the permanganate in a medium with higher alkalinity. Higher loading of barium peroxide or hydroxide increases the alkalinity of the system and

results in more MnO_2 being oxidized and thus lowers the catalytic activity towards the decomposition of sodium chlorate.

Barium hydroxide has a higher inhibiting effect than the peroxide. This is probably due to the fact that barium hydroxide starts melting at a relatively low temperature of 370°C . Once melted, it has a better contact with sodium chlorate and the metal oxides and thus has a stronger interaction.

Manganese(IV) oxide, nickel(II) oxide and copper(II) oxide are all active catalysts for the decomposition of sodium chlorate, and barium peroxide and hydroxide are moderately active catalysts as reported [6]. When two catalysts are used together, one would assume that the total catalytic effect would be higher than for either one of the catalysts used alone, or at least would show an activity close to the activity of the more active one. It is interesting to see that the catalytic activities of the transition metal oxides are quenched by barium peroxide and hydroxide. This can be explained based on the catalytic mechanism previously proposed [8].

The metal cations, Mn^{4+} , Ni^{4+} , and Cu^{2+} , on the surfaces, edges and defect sites of the metal oxide crystallites have lower coordination number than the metal cations in the body of the crystallite. For example, NiO has a rock salt structure, and each Ni^{2+} cation is octahedrally coordinated by six O^{2-} ions and each O^{2-} ion is octahedrally surrounded by six Ni^{2+} ions. Therefore, each $\text{Ni}^{2+}-\text{O}^{2-}$ bond has the strength of $1/3$ of a single chemical bond according to Pauling's crystallographic principle [10]. Each Ni^{2+} ion on the surface may be coordinated by only five O^{2-} . The total negative charge it attracts from the five O^{2-} ions are $5/3 e^-$. In order to keep electrically neutral, it must attract oxygen from air or from the chlorate group and thus behave as a Lewis acid site. Ni^{2+} ion also has unfilled valence d-orbitals to accept extra electrons. In the edges or other defect sites, an Ni^{2+} cation may be coordinated by even fewer than five oxygen anions and thus has even higher tendency to attract oxygen. Each of the oxygen atoms in the ClO_3^- group has two unshared electron pairs. It can donate an electron pair to an unsaturated metal cation to form a surface complex and behave as a Lewis base. Formation of the coordination bonds between the metal cation and the oxygen from the chlorate group weakens the oxygen–chlorine bond and facilitates the decomposition of the chlorate. Barium peroxide and hydroxide, however, are stronger bases. They can compete for the metal cation sites on the oxide surface and thus inhibit the catalytic effect.

The DTA traces for sodium chlorate, mixtures of sodium chlorate with MnO_2 , NiO and CuO, and mixtures of sodium chlorate containing 2% barium peroxide with MnO_2 , NiO and CuO are given in Fig. 1. The DTA trace of sodium chlorate alone has two peaks. The endothermic peak at 260°C is the melting of sodium chlorate. The broad exothermic peak at 580°C consists of two peaks caused by the decomposition of sodium chlorate and the sodium perchlorate formed through disproportionation [6]. In the absence of catalysts, sodium chlorate decomposes at a temperature much higher than its melting temperature, that is, in the liquid state.

When catalyzed by MnO_2 , NiO or CuO, the melting temperature of sodium chlorate is basically unchanged. The exothermic peaks, however, all move to the lower temperature side and become partially overlapped with the endothermic peaks as shown by curves 2, 4 and 6. This indicates that the sodium chlorate starts decomposing

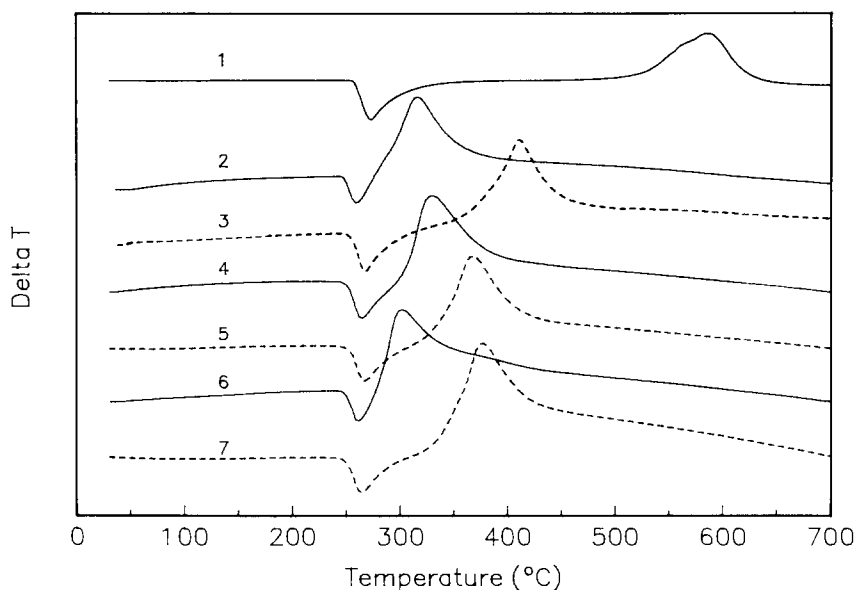


Fig. 1. DTA plots of thermal decomposition of NaClO_3 catalyzed by metal oxides in the presence and absence of BaO_2 : 1, NaClO_3 alone; 2, 4% MnO_2 ; 3, 4% MnO_2 and 2% BaO_2 ; 4, 4% NiO ; 5, 4% NiO and 2% BaO_2 ; 6, 4% CuO ; and 7, 4% CuO and 2% BaO_2 .

before complete melting. When 2% barium peroxide is added to the sodium chlorate with metal oxide mixture, however, the exothermic peaks move to the higher temperature side and become separated from the endothermic peaks. The sodium chlorate again decomposes in the liquid stage. Decomposing in the liquid phase is beneficial for applications such as chemical oxygen generators [6]. Barium hydroxide produces similar effects to those shown in Fig. 1.

Nickel(II) oxide is unique among the three transition metal oxides studied. It has high catalytic activity and it has the lowest sensitivity to barium peroxide and hydroxide loading. Therefore, it may be a good candidate to be studied for use in chemical oxygen generating devices.

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