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Catalytic effects of metal oxides on the thermal decomposition of sodium chlorate

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Abstract

The thermal decomposition of $NaClO_3$ in the presence of metal oxides was studied using thermogravimetric analysis. A number of metal oxides were prepared to have comparable surface areas, and their catalytic effects on $NaClO_3$ decomposition were compared. It was found that the catalytic activity depends on the electron configurations of the metal cations. Oxides containing metal cations with partially filled d-orbitals are all active catalysts for $NaClO_3$ decomposition. Transition metal cations with no d-electrons are moderately active. Metal oxides containing metal cations with completely filled d-orbitals or noble gas configurations have very little activity.

INTRODUCTION

Alkali metal chlorates and perchlorates can generate oxygen upon decomposition. The thermal decomposition of alkali metal chlorates and perchlorates catalyzed by metal oxides has been extensively studied [1–12]. Several different relative catalytic activity sequences of the metal oxides have been reported. Inconsistent or even contradictory catalytic mechanisms have been proposed based on the relative catalytic activities of the metal oxides.

Rudloff and Freeman reported that Cr_2O_3, CoO and Co_3O_4 are the most active catalysts for the decomposition of $KClO_3$ and $KClO_4$ [5]. They considered that only p-type semiconductors are active catalysts, and this view was shared by some [6, 7, 13]. But other authors observed different results and have different opinions. Shimokawabe et al. found that Cr_2O_3, MnO_2, and Fe_2O_3 have the highest activities toward $KClO_4$ decomposition, and assumed that metals oxides with higher electrical conductivities have higher activities [8]. Said et al. [9] found that Cr_2O_3 and Co_3O_4 are the most active catalysts. They suggested that metal oxides that are p-type

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semiconductors and can change to n-type semiconductors are effective catalysts [9]. Iwakura et al. found that Co_3O_4 and Fe_2O_3 are the most active catalysts [10]. They proposed that the catalytic activity is related to electron hopping. Metal oxides with lower activation energies for the hopping process have higher activities. Morishima et al. reported that NiO is the most active catalyst [11]. They also considered that the catalytic activity is related to electron hopping. Feng et al. found MnO_2 and Fe_2O_3 to be the most active catalysts and suggested that metal oxides containing metal cations with half-filled d-orbitals are likely to have high activities [12].

The inconsistent results of the previous studies are probably caused by differences in the surface areas of the metal oxides, because the metal oxides used in the previous studies were from different sources and were not characterized for surface areas or particle sizes. It is the purpose of this study to prepare metal oxides with comparable surface areas, and to compare their relative activities toward the thermal decomposition of sodium chlorate. The correlations between the catalytic activities and the electron configurations of the metal cations in the oxides will be discussed based on the relative activities.

EXPERIMENTAL METHODS

Chromium oxide was prepared by decomposing chromium(III) acetate hydroxide ($Cr_3(OH)_2(OOCCH_3)_7$) at 425°C. Iron oxide sample 1 was prepared by decomposing iron oxalate ($FeC_2O_4 \cdot 2H_2O$) at 350°C. Nickel oxide and zinc oxide were prepared by decomposing nickel carbonate hydroxide ($NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$) and zinc carbonate hydroxide ($ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$) at 450 and 255°C, respectively. Manganese oxide sample 1 and copper oxide were prepared by decomposing the corresponding carbonates at 450 and 260°C, respectively. Cobalt oxide samples 1 and 2 were prepared by decomposing cobalt carbonate at 350 and 800°C, respectively. ZrO_2 was prepared by heating zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot 4H_2O$) at 500°C. CaO and La_2O_3 were prepared by heating the corresponding hydroxides at 650 and 550°C, respectively. The oxide products were analyzed by X-ray diffraction using a Rigaku D/maxII diffractometer.

MgO, SiO_2, SnO_2, MnO_2 sample 2 and Fe_2O_3 sample 2 were purchased from chemical suppliers. CeO_2, as purchased, was heated at 650°C to reduce its surface area. Sodium chlorate, as purchased, was in the form of crystalline particles.

Specific surface areas were measured using the multi-point measurement method with a BET sorptometer. Each of the samples was heated at 150°C in vacuum to drive off moisture and adsorbed gases prior to the measurements. Nitrogen was used as the adsorbent gas.

Each of the oxides was mixed with $NaClO_3$ in a molar ratio of 4% corresponding to a ratio of one mole of metal cations to 24 mol of $NaClO_3$. Each of the mixtures was mixed thoroughly with a mortar and pestle.

Thermogravimetric (TG) analysis was carried out using a Netzsch thermal analyzer Model STA 409. Approximately 100 mg of sample was heated up at 20°C min^{-1} to 700°C in an oxygen stream of 150 ml min^{-1}.

RESULTS AND DISCUSSION

The metal oxides prepared were identified by X-ray diffraction analysis as CaO, Cr_2O_3, MnO_2, Fe_2O_3, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, ZrO_2, and La_2O_3. The surface areas of all the metal oxides are given in Table 1. MgO, ZrO_2, MnO_2 sample 1, Fe_2O_3 sample 1, Co_2O_4 sample 1, NiO, CuO, and ZnO all have surface areas of around 60 m^2 g^{-1}. This provides a good basis for comparing the relative activities. The lower surface area of Cr_2O_3 may not be relevant, because the evidence discussed later on suggests that $NaClO_3$ catalyzed by Cr_2O_3 decomposes through a different process. The surface areas of CaO, CeO_2, La_2O_3, SiO_2, and SnO_2 are lower and comparable to the surface area of Co_3O_4 sample 2.

The effects of surface areas on the catalytic activities of metal oxides are demonstrated by thermogravimetric analysis in Fig. 1. The TG curves of $NaClO_3$ catalyzed by MnO_2 samples 1 and 2, and Fe_2O_3 samples 1 and 2 are compared with that of uncatalyzed $NaClO_3$ decomposition. Because the decomposition onset temperatures are relatively difficult to determine unambiguously, the temperatures at which 50% of the $NaClO_3$ has decomposed (50% DT) and the final decomposition temperatures are used to compare the relative activities of the metal oxides. The 50% DTs of $NaClO_3$ catalyzed by MnO_2 sample 1, Fe_2O_3 sample 1, Fe_2O_3 sample 2 and MnO_2 sample 2 are 305, 335, 378, and 542°C respectively, compared to a 50% DT of 565°C for the uncatalyzed decomposition of $NaClO_3$.

TABLE 1

BET surface areas of the metal oxides

Compounds	Surface area/m^2 g^{-1}	Compounds	Surface area/m^2 g^{-1}
MgO	67	MnO_2 (2)	0.5
MnO_2 (1)	58	Fe_2O_3 (2)	8
Fe_2O_3 (1)	59	CeO_2	6
Co_3O_4 (1)	61	CaO	7
NiO	62	SiO_2	6
CuO	63	SnO_2	6
ZnO	68	Co_3O_4 (2)	5
ZrO_2	68	La_2O_3	5
Cr_2O_3	41		

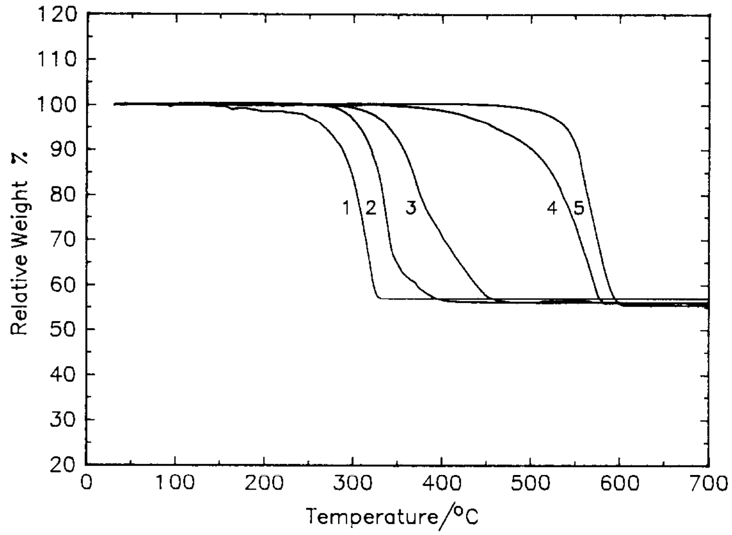

Fig. 1. TG curves of $NaClO_3$ catalyzed by metal oxides with different surface areas. (1) MnO_2 sample 1, (2) Fe_2O_3 sample 1, (3) Fe_2O_3 sample 2, (4) MnO_2 sample 2, and (5) no catalyst.

MnO_2 sample 1 is more active than Fe_2O_3 sample 1, as indicated by its 30°C lower 50% DT value. MnO_2 sample 2, however, is far less active than Fe_2O_3 sample 2. Fe_2O_3 sample 2 is still an active catalyst, but MnO_2 sample 2 has very little activity. The 50% DT of $NaClO_3$ catalyzed by MnO_2 sample 2 is 164°C higher than that of $NaClO_3$ catalyzed by Fe_2O_3 sample 2. This is consistent with the fact that Fe_2O_3 sample 2 has a surface area of $8\,m^2\,g^{-1}$ whereas MnO_2 sample 2 has a surface area of only $0.5\,m^2\,g^{-1}$. This crossover indicates that changes in surface area can have a greater effect than the activity difference between different metal oxides. Therefore, it is not meaningful to compare relative activities of metal oxides with unknown surface areas. The catalytic mechanisms based on the relative activity sequence of metal oxides with unknown surface areas can be misleading.

The TG profiles of $NaClO_3$ with 4 mol.% of the high surface area metal oxides are compared in Fig. 2. It is evident that cobalt oxide is the most active oxide catalyst for $NaClO_3$ decomposition. The 50% DT is 255°C. MnO_2 sample 1, CuO, NiO, and Fe_2O_3 sample 1 are also very active, although not as active as Co_3O_4. The 50% DTs of $NaClO_3$ catalyzed by CuO, MnO_2, NiO, and Fe_2O_3 are 305, 305, 325, and 330°C respectively. ZnO and MgO have very low activities. The 50% DTs of $NaClO_3$ containing ZnO and MgO are 535 and 550°C respectively, compared to a 50% DT of 565°C for uncatalyzed $NaClO_3$. ZrO_2 is moderately active. The 50% DT of $NaClO_3$ catalyzed by ZrO_2 is 430°C.

The decomposition of $NaClO_3$ catalyzed by Cr_2O_3 is a two-step process. The first step, between 210 and 225°C, is a chemical reaction between

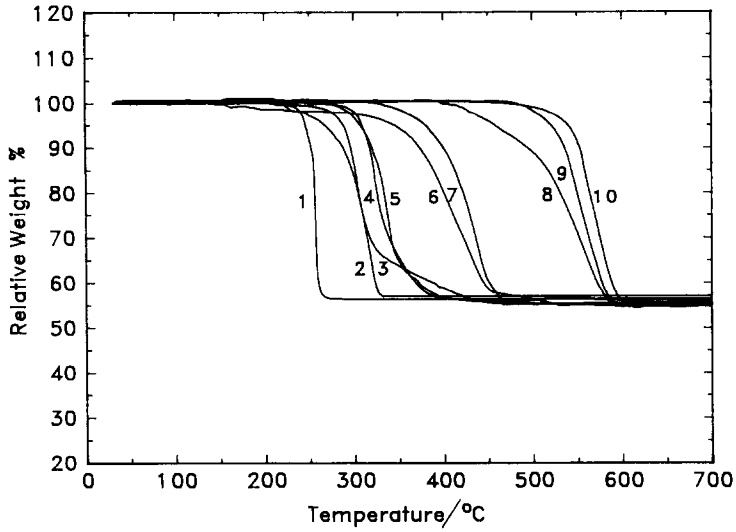

Fig. 2. TG curves of $NaClO_3$ catalyzed by metal oxides with high, comparable surface areas. (1) Co_3O_4 sample 1, (2) MnO_2 sample 1, (3) CuO, (4) Fe_2O_3 sample 1, (5) NiO, (6) Cr_2O_3, (7) ZrO_2, (8) ZnO, (9) MgO, and (10) no catalyst.

Cr_2O_3 and $NaClO_3$ to producing $Na_2Cr_2O_7$, NaCl and ClO_2, rather than a catalytic decomposition [14]. The second step, between approximately 350 and 500°C, is the decomposition of $NaClO_3$ catalyzed by the $Na_2Cr_2O_7$ formed in the first step. The fact that the first decomposition step starts at about 210°C has led to the suggestion that Cr_2O_3 is the most active catalyst [6, 8, 9].

Because high surface area SiO_2, SnO_2, CaO, La_2O_3, and CeO_2 were not available at the time of this study, the catalytic effects of SiO_2, SnO_2, CaO, La_2O_3, and CeO_2 with surface areas of around 5 $m^2\,g^{-1}$ are compared with the effects of low surface area Co_3O_4 sample 2 in Fig. 3. As shown in Table 1, the surface areas of the oxides involved in Fig. 3 are all comparable.

Co_3O_4 sample 2 has a surface area of only 5 $m^2\,g^{-1}$. It is still very active, although not as active as Co_3O_4 sample 1 as shown in Fig. 2. The 50% DT of $NaClO_3$ catalyzed by Co_3O_4 sample 2 is 350°C. SiO_2 has no activity on the decomposition. Actually, the final temperature of the decomposition is higher in the presence of SiO_2 than when uncatalyzed. The mixture of $NaClO_3$ and SnO_2 starts losing weight at approximately 400°C, but the decomposition proceeds very gradually. The final decomposition temperature is also higher than that of the uncatalyzed decomposition. Therefore, both SiO_2 and SnO_2 behave as inhibitors rather than catalysts. CaO is slightly active, and the 50% DT of $NaClO_3$ catalyzed by CaO is about 30°C lower than that of the uncatalyzed decomposition. Just like ZrO_2, La_2O_3 and CeO_2 are also moderately active. The 50% DTs of $NaClO_3$ catalyzed by La_2O_3 and CeO_2 are 445 and 465°C, respectively.

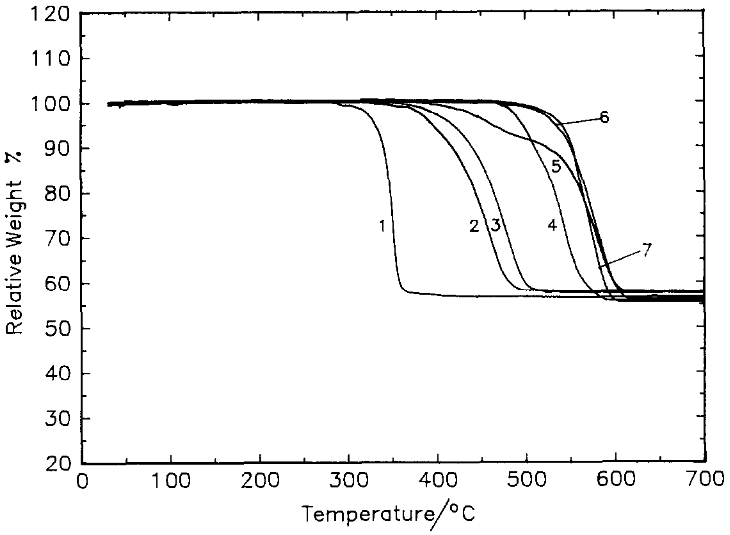

Fig. 3. TG curves of $NaClO_3$ catalyzed by metal oxides with comparable surface areas. (1) Co_3O_4 sample 2, (2) La_2O_3, (3) CeO_2, (4) CaO, (5) SnO_2, (6) SiO_2, and (7) no catalyst.

Fe_2O_3 is an n-type semiconductor. MnO_2 is also an n-type semiconductor below 400°C [15]. These two oxides are as active as the p-type semiconductors CuO and NiO, as shown in Fig. 2. Therefore, an active oxide is not necessarily a p-type semiconductor.

The catalytic activity is not related to conductivity either. SnO_2 is an n-type semiconductor with very high conductivity compared to Co_3O_4 and Fe_2O_3 (Table 2), but it has very little activity. NiO has very low conductivity at room temperature, but it is very active. Therefore, electrical conductivity or n-type semiconductivity cannot be a measure of the catalytic activity either.

It has been proposed that the catalytic activities of metal oxides are related to the activation energies for electrical conductivity [10, 11]. Metal oxides with lower activation energies have higher activities. The activation energies of electrical conductivity of some metal oxides are also given in Table 2. It appears that the activation energy cannot be a reasonable measure of the catalytic activity. SnO_2 and CuO have the same activation energy. But they have very different activities. La_2O_3 has the highest activation energy among all the oxides used in this study, but it is a moderately active catalyst. MgO and SiO_2 both have activation energies not much higher than that of NiO, but both of them show only minimum activities compared to NiO.

It appears that the catalytic activities ae related to the interaction between the ClO_3^- anions and the metal cations in the oxides. This interaction can be explained using NiO as an example. NiO has the NaCl structure. Each Ni^{2+} cation is octahedrally coordinated with six oxygen

TABLE 2

Resistivities and activation energies for electrical conductivity of some metal oxides

Oxides	Resistivity/ohm m	Activation energy/eV
MgO	9×10^9 (500°c)	1.16
SiO_2	1×10^4 (700°C)	1.32
NiO	1×10^{11} (20°C)	0.93
CuO	1–10 (20°C)	0.70
ZnO	94.4 (160°C)	
SnO_2	4×10^{-4} (20°C)	0.70
La_2O_3	1×10^6 (560°C)	2.86
CeO_2	1×10^4	2.7
ZrO_2	700 (600°C)	
Fe_2O_3	62.4 (570°C)	
Co_3O_4	100	
MnO_2	1×10^{-5}	0.30

Temperatures at which the resistivities were measured are given in parentheses [16].

ions. On the surface, especially on the edges, vertices, and structural defect sites of the crystallites, Ni^{2+} may be coordinated by only five or even fewer oxygen ions. These unsaturated Ni^{2+} cations tend to attract ligands to form a stable octahedral coordination. The same process can also happen to other transiton metal oxides with different structures and coordination numbers. Because only the metal cations are involved, it is not surprising that $Na_2Cr_2O_7$, a non-oxide compound, is also moderately active.

The catalytic activities of metal cations appear to be determined by their electron configurations. The metal cations involved in the oxides used in this study can be divided into three groups. The first group consists of metal cations with partially filled d-orbitals, MnO_2, Fe_2O_3, Co_3O_4, CuO, and NiO. These oxides are all very active. The second group consists of metal oxides containing cations with noble gas configurations or with completely filled d-orbitals (d^{10}), MgO, CaO, SiO_2, ZnO, and SnO_2. These oxides have the lowest activities. The third group includes metal oxides containing transition metal cations with completely empty d-orbitals (d^0), ZrO_2, La_2O_3 and CeO_2. These oxides are moderately active. It is interesting to note that Cr^{6+} also has completely empty d-orbitals and accordingly shows a moderate activity similar to the activities of ZrO_2, La_2O_3 and CeO_2.

Metal cations with partially filled d-orbitals have unfilled valence orbitals. These cations have relatively small sizes because of less electrical shielding. Therefore, they have a higher tendency to attract extra electrons and behave as Lewis acid sites. Each of the oxygen atoms in the chlorate group ClO_3^- has unshared electron pairs and can behave as a Lewis base. Therefore, the oxygen can donate one of the unshared electron pairs into the empty valence orbitals of the metal cation, and thereby form a surface complex. Formation of the M^{n+}–O coordination bond weakens the O–Cl bond in the ClO_3^- group and results in chlorate decomposition.

Oxides containing cations with noble gas or d^{10} configurations, however, are spherical and have the lowest energies. Their positive electrical fields are effectively shielded by electrons. In addition, in order to form the coordination bond, an electron pair from the chlorate will have to go into higher energy orbitals, which is not favored from the formation of the complex. Both of these factors makes it difficult to form coordination bonds. Therefore, all oxides with cations in this group have very low activities.

Transition metal cations with d^0 cations are also spherical and have low energies, like the second group of cations. But they have empty d-orbitals to accommodate the electron pairs from the chlorate. This can facilitate the formation of the coordination bonds. Therefore, d^0 transition metal cations are more active than cations with d^{10} or noble gas configurations, and less active than cations with partially filled d-orbitals.

In conclusion, the catalytic activity of a metal oxide toward the decomposition of sodium chlorate is determined by the electron configuration of the metal cation rather than the electronic properties of the oxide. Metal cations with partially filled d-orbitals are all very active. Transition metal cations with d^0 configurations are moderately active. And metal cations with d^{10} or noble gas configurations have only minimal activities.

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