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Catalytic effects of metal oxides on the decomposition of Potassium perchlorate

Yunchang Zhang *, Girish Kshirsagar, John E. Ellison, James C. Cannon

Nellcor Puritan Bennett Corp., 10800 Pflumm Road, Lenexa, KS 66215, USA

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Abstract

Catalytic effects of metal oxides with comparable surface areas on the decomposition of potassium perchlorate were studied by thermogravimetric analysis. The catalytic mechanism is discussed based on the relative activity of the metal oxides. It is found that the oxides containing transition metal cations with partially filled d-orbitals have the highest activities, the oxides containing transition metal cations with completely empty valence d-orbitals are moderately active, and the oxides containing metal cations with completely filled d-orbitals or noble gas configurations have the lowest activities. Differences between the decomposition of potassium perchlorate and the previously reported decomposition of sodium chlorate are explained by differences in the melting points and molecular structures of these salts.

Keywords: Catalytic decomposition; Potassium perchlorate

1. Introduction

A number of papers have reported the catalytic effects of metal oxides on the decomposition of potassium perchlorate and have proposed catalytic mechanisms [1-7]. Nearly all of them have emphasized the effects of the physical properties rather than the chemical properties of the metal oxides on the catalytic activity. Inconsistent results have been reported and contradictory catalytic mechanisms have been proposed.

Based on the relative activity of 14 different metal oxides on the decomposition of $KClO_4$, Rudloff and Freeman [1] concluded that metal oxides that are p-type

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* Corresponding author.

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semiconductors are active catalysts for the decomposition of potassium chlorate and perchlorate, even though they admitted that the n-type semiconductor α-Fe_2O_3 also has high activity. This conclusion is shared by Haralambous et al. [2] who found that the mixed oxide of nickel and chromium annealed at higher temperatures has a lower p-type conductivity and a lower catalytic activity toward the decomposition of potassium perchlorate, and thus concluded that p-type oxides are active catalysts. The fact that samples annealed at higher temperatures have lower surface areas was overlooked. It was reported that the nonoxide compounds, such as cobalt chloride, manganese chloride and nickel sulfate, have a catalytic activity similar to that of the corresponding oxides for the decomposition of sodium chlorate [3]. It is unlikely that these nonoxide compounds are p-type semiconductors and have similar hole concentrations to those of the corresponding oxides.

It was also proposed that in order to be an active catalyst, a metal oxide must be a p-type semiconductor which can change to an n-type semiconductor at the decomposition temperature [4,5]. Based on the relative activity of 12 metal oxides, Shimokawabe et al. [6] concluded that metal oxides with high conductivity, regardless of whether they are p-type or n-type, have high activity. Collins [7] also reported that the catalytic activity generally increases with increasing p-type semiconductivity. However, he concluded that no significant trend can be unequivocally established and further study is needed to explain the activity of n-type semiconductors.

Nagaishi et al. [8] found that Cr_2O_3, Cu_2O, and BaO have high activity, and NiO has little activity, for the decomposition of potassium perchlorate, and concluded that in order to be a catalyst, a metal oxide must be able to react with potassium perchlorate or to go through double decompositions.

The contradictory results reported and mechanisms proposed by previous authors are likely due to differences in the surface areas of the metal oxides they used. Our previous work has indicated that the surface area of a metal oxide can have a crucial effect on its catalytic activity and it is not very meaningful to compare the relative activity of different oxides without knowing their surface area [9]. The same work also indicated that the electron configuration of a metal cation determines its catalytic activity towards the decomposition of sodium chlorate. It is the purpose of this study to compare the relative catalytic activity of metal oxides toward the decomposition of potassium perchlorate and to see whether the catalytic process is parallel to that of sodium chlorate decomposition.

2. Experimental methods

Iron oxide 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°C and 255°C respectively. Manganese oxide and copper oxide were prepared by decomposing the corresponding carbonates at 450 and 260°C respectively. Cobalt oxide was prepared by decomposing cobalt carbonate at 350°C. A part of the cobalt oxide thus prepared was then annealed at 750°C to produce a low surface area cobalt oxide. Zirconium oxide was prepared by decomposing zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot 4H_2O$) at 500°C. Calcium oxide and lanthanum oxide were prepared by heating the corresponding hydroxides at 650 and 550°C respectively. The oxide products were analyzed through X-ray diffraction using a Rigaku Diffractometer D/maxII.

Magnesium oxide and silicon oxide were purchased from Aldrich Chemicals. Cerium oxide, as purchased from Johnson and Mathey, and aluminum oxide, as purchased from Aldrich Chemical, were annealed at 550 and 750°C respectively to reduce the surface areas. Potassium perchlorate, 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 adsorbate gas.

Each of the oxides was mixed with potassium perchlorate in a molar ratio of 4%, corresponding to a ratio of one mole of metal cations to 24 mole of potassium perchlorate. Each of the mixtures was intimately mixed using a mortar and pestle. Thermogravimetric (TG) analysis was carried out using a Netzsch Thermal Analyzer Model STA 409. Aluminum oxide sample crucibles were used. The aluminum oxide is inert and does not catalyze the decomposition of the perchlorate. The sample temperature was calibrated by the decomposition temperatures of calcium oxalate. 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}.

3. Results and discussion

The metal oxides prepared were verified through X-ray diffraction analysis as CaO, La_2O_3, MnO_2, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO and ZrO_2, and their surface areas were 7, 5, 58, 59, 61, 62, 63, 68 and 68 $m^2\ g^{-1}$ respectively. Except for calcium oxide and lanthanum oxide, the surface areas of these metal oxides are all relatively high and comparable. This provides a consistent basis for comparing the relative activity of the high surface area oxides. The surface areas of CeO_2, SiO_2, and SnO_2 were 6 $m^2\ g^{-1}$ and that of the low surface area cobalt oxide was 5 $m^2\ g^{-1}$. The low surface area cobalt oxide was used as a reference to compare the relative activity of the low surface area oxides. X-ray diffraction analysis verified that the lower surface area cobalt oxide prepared at 750°C was still Co_3O_4.

The TG profiles of potassium perchlorate with 4 mol% of the high surface area metal oxides are compared with the decomposition of potassium perchlorate alone in Fig. 1, and the TG profiles of potassium perchlorate catalyzed by low surface area oxides are given in Fig. 2. Since the onset decomposition temperature is relatively hard to determine, the temperature at which 50% of the perchlorate has decomposed is used to compare the relative activity of the oxide additives and is referred to as 50% DT. The 50% DT can be determined within ±3°C. The 50% DTs of the samples of potassium perchlorate with the metal oxide catalysts are summarized in Table 1 and the 50% DTs

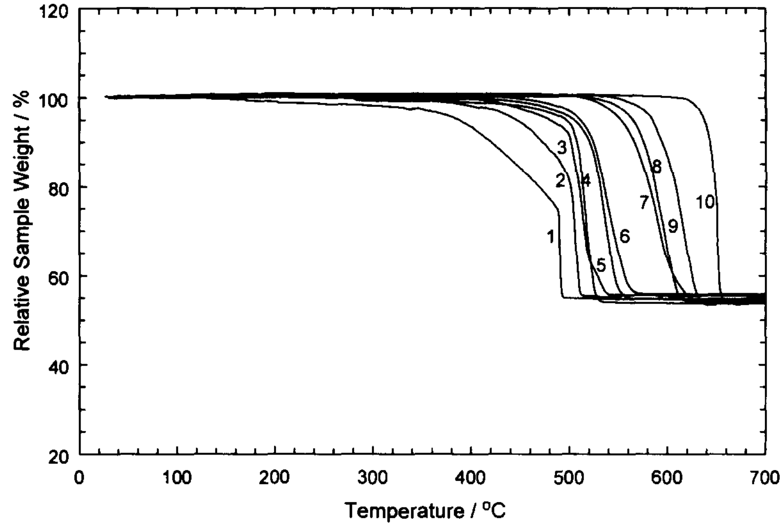

Fig. 1. Thermogravimetric analysis of $KClO_4$ catalyzed by metal oxides with high and comparable surface areas; 1, Co_3O_4; 2, NiO; 3, CuO; 4, MnO_2; 5, Fe_2O_3; 6, ZrO_2; 7, Al_2O_3; 8, MgO; 9, ZnO; and 10, no catalyst.

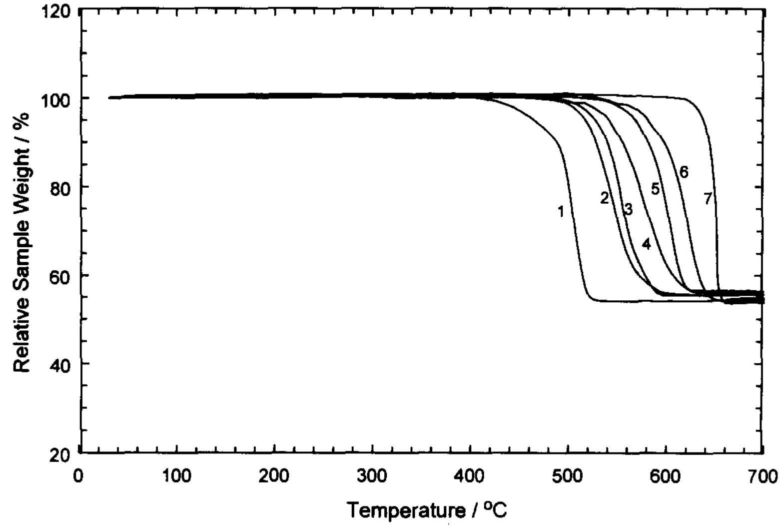

Fig. 2. Thermogravimetric analysis of $KClO_4$ catalyzed by metal oxides with comparable surface areas: 1, low surface area Co_3O_4; 2, La_2O_3; 3, CeO_2; 4, CaO; 5, SnO_2; 6, SiO_2; and 7, no catalyst.

of sodium chlorate catalyzed by these same oxides reported previously [9] are also given in the table for comparison.

The two figures show that the relative catalytic activity of the metal oxides toward the decomposition of potassium perchlorate is generally parallel to their relative activity toward the decomposition of sodium chlorate reported previously [9]. Transi-

Table 1
Catalytic effects of metal oxides on the decomposition of $KClO_4$ and $NaClO_3$

	Effects on $KClO_4$		Effects on $NaClO_3$ [9]	
	50% DT/°C	Reduction of 50% DT/°C	50% DT/°C	Reduction of 50% DT/°C
No catalysts	650	n/a	561	n/a
4% SiO_2	616	34	564	−3
4% ZnO	612	38	535	26
4% SnO_2	597	53	561	0
4% MgO	589	61	546	11
4% Al_2O_3	585	65	n/a	n/a
4% CaO	575	75	531	30
4% CeO_2	554	96	465	96
4% La_2O_3	544	106	445	116
4% ZrO_2	538	112	430	131
4% Fe_2O_3	533	117	330	231
4% MnO_2	515	135	305	256
4% CuO	511	139	305	256
4% Co_3O_4[a]	508	142	350	211
4% NiO	503	147	325	236
4% CO_3O_4	480	170	255	306

[a] Low surface area sample.

tion metal oxides have higher activities than the oxides of the main group elements. The metal oxides can be roughly divided into three groups according to their activities. The high activity group includes the oxides of cobalt, nickel, copper, manganese and iron. Oxides of this group can reduce the 50% DT of potassium perchlorate by 117–170°C. The low activity group includes the oxides of calcium, aluminum, magnesium, tin, silicon and zinc. Oxides in this group have lower but still significant catalytic activities and they can lower the 50% DT of potassium perchlorate by 34–75°C. The medium activity group includes the oxides of zirconium, lanthanum and cerium. The oxides in this group are moderately active and they can reduce the 50% DT by 96–112°C respectively.

The low surface area cobalt oxide has lower activity than the high surface area one. The sample of potassium perchlorate with 4% of the low surface area cobalt oxide has a 50% DT at 508°C which is higher than the 50% DT of 480°C for the sample mixed with high surface area cobalt oxide and is even higher than the 50% DT of 503°C for the sample of potassium perchlorate with nickel oxide. This further indicates that comparing the relative activity of metal oxides with unknown or different surface areas can be misleading.

It appears that the catalytic activity of a metal oxide does not depend on its semiconductivity or conductivity. Fe_2O_3 is an n-type semiconductor and MnO_2 is an n-type semiconductor below 400°C [10]. Both of these two oxides have fairly high catalytic activities. Manganese dioxide has about the same activity as the p-type semiconductors copper oxide and nickel oxide and the decomposition of the potassium perchlorate with manganese dioxide starts below 400°C, as shown in Fig. 1. Therefore, an active oxide is not necessarily a p-type semiconductor. Nor is the catalytic activity related to electrical conductivity. Tin dioxide and zinc oxide are both n-type semiconductors with high conductivities compared to the oxides of cobalt, lanthanum, cerium and calcium [11]. However, their activities are much lower than those of the latter oxides. The activities of tin dioxide and zinc oxide are even lower than those of the typical insulators such as aluminum oxide and magnesium oxide. Therefore, the catalytic activity cannot be explained by and is not related to the electrical conductivity.

The results presented above appear to support the explanation we proposed previously [9] that the catalytic activity of a metal oxide is determined by the electron configuration of the metal cation. The catalytic process is a process of forming a surface complex between the metal cation and the perchlorate anion. The metal cations on the surface of the oxides are electrically unsaturated and tend to attract extra electrons or negative charges. The oxygen atoms in the perchlorate anion have unshared electron pairs and can donate one or more of the unshared pairs to the metal cation and act as ligands. This interaction can weaken the oxygen–chlorine bond in the perchlorate anion and thus can facilitate the decomposition of the perchlorate.

The ability of a metal cation to form coordination bonds depends on its electron configuration. Therefore, the catalytic activity of a metal oxide is determined by the electron configuration of its metal cation. The metal cations in the high activity group of the metal oxides all have partially filled d-orbitals. The metal cations in the medium activity group of oxides are all transition metal cations with completely empty valence d-orbitals (d^0) such as ZrO_2, La_2O_3 and CeO_2. The metal cations in the low activity group of oxides all have either noble gas configurations or completely filled valence d-orbitals (d^{10}), such as MgO, SiO_2, ZnO, and SnO_2.

Metal cations with partially filled d-orbitals have unfilled valence orbitals. These cations are relatively small in size because there is less electrical shielding. Therefore, they have a higher tendency to attract extra electrons and to form surface coordination bonds with the oxygen atom in the perchlorate anion, and thus have high activities. In addition, all these transition metal cations have variable oxidation states in the oxides, which can accommodate the adsorption and desorption of oxygen and thus facilitate the decomposition of the perchlorate. The metal cation can form a bond with an oxygen atom in the perchlorate group and increase its oxidation state. After the oxygen–chlorine bond is broken, the oxide can allow the oxygen to desorb by lowering the oxidation state of the metal cation.

Oxides containing cations with noble gas or d^{10} configurations, however, are spherical and their positive electrical fields are effectively shielded by electrons. In addition, in order to form the coordination bond, an electron pair from the perchlorate would have to go into higher energy orbitals, which does not favor the formation of the complex. Both of these factors make it difficult to form coordination bonds. Therefore, all oxides with cations in this group should have low activities.

Transition metal cations with d^0 configurations are also spherical. But they have empty d-orbitals to accommodate the electron pairs from the perchlorate, which can facilitate the formation of the coordination bonds. Therefore, oxides containing d^0

transition metal cations are more active than the oxides containing cations with d^{10} or noble gas configurations and less active than oxides containing cations with partially filled d-orbitals.

Fe_2O_3 is a transition metal oxide containing metal cations with partially filled d-orbitals but its activity is lower than those of the other transition metal oxides containing metal cations with partially filled d-orbitals. This is probably related to the unique electron configuration of the Fe^{3+} ion. Fe^{3+} has five d-electrons and is in the high-spin state with spherical symmetry. The electron pair it attracts will have to go to the outer orbitals with higher energy levels, which is less favored. Therefore, Fe_2O_3 has an activity that is closer to the activities of the medium activity group.

Co^{3+} has a $3d^6$ configuration and is always in the low-spin state. In an octahedral field, all the six d-electrons stay in the low-energy t_{2g} orbitals and the empty e_g orbitals can accommodate extra electrons attracted from the oxygen in the perchlorate anion. This may be the reason why cobalt oxide has the highest activity among all the metal oxides used in this study.

Even though the trends and relative activity sequences of the metal oxides toward the decomposition of potassium perchlorate and sodium chlorate are generally similar, there are some obvious differences in the effects that each oxide has on the perchlorate and the chlorate, as compared in Table 1. All the oxides used in this study brought down the perchlorate decomposition temperature significantly. Even the least active, SiO_2, can lower the 50% DT by 34°C. The reduction in 50% DT of potassium perchlorate by calcium oxide, magnesium oxide, and zinc oxide are 75, 61, and 38°C respectively compared to 30, 11, and 26°C reduction for the 50% DT of sodium chlorate [9]. While SnO_2 and SiO_2 reduce the 50% DT of potassium perchlorate by 53 and 34°C respectively and behave as catalysts, they do not catalyze, and may even inhibit, the decomposition of sodium chlorate.

The differences described above can be explained in terms of the differences between potassium perchlorate and sodium chlorate. The chlorine atom in the perchlorate anion forms four covalent bonds with four oxygen atoms and forms a stable structure as indicated by higher melting and decomposition temperature. Attraction of any one of the oxygen atoms from the perchlorate anion can weaken the bond and facilitate the decomposition. Therefore, all the metal oxides have significant catalytic effect for potassium perchlorate. The chlorine atom in the chlorate anion forms only three covalent bonds with three oxygen atoms and has one unshared electron pair. A metal cation can attract one of the oxygen atoms and thus catalyzes the decomposition of the chlorate. However, it can also attract the unshared electron pair from the chlorine atom and thus reinforces the chlorine–oxygen bond and inhibits the decomposition. It has been reported that when the decomposition of sodium chlorate is mixed with acidic oxides, such as V_2O_5 and MoO_3, much more chlorine is generated together with oxygen [12]. This is an indication that acidic oxides may attract the chlorine atom in the chlorate anion. SiO_2 and SnO_2 are both acidic and they may attract the chlorine atom in the chlorate anion. Therefore, they show little catalytic effect or even inhibit the decomposition of sodium chlorate.

The catalytic activities of the high activity group of transition metal oxides toward the decomposition of potassium perchlorate are significantly lower than toward the decomposition of sodium chlorate. For example, 4% cobalt oxide can lower the 50% DT of sodium chlorate by 306°C and it can only lower the 50% DT of potassium perchlorate by 170°C. This difference is probably due to the fact that the perchlorate has a much higher melting temperature. Sodium chlorate starts melting at about 250°C. Most of the sodium chlorate decomposes in the liquid phase. The molten sodium chlorate has much better contact with the transition metal oxides and the decomposition, therefore, proceeds rapidly. Potassium perchlorate, on the other hand, does not melt until about 600°C. Therefore, a large portion of potassium perchlorate decomposes in the solid state even when catalyzed by the transition metal oxides. The potassium perchlorate has to migrate through the potassium chloride layer formed to come into contact with the metal oxide catalyst and thus the decomposition is much slower. The TG trace of potassium perchlorate with cobalt oxide shows clearly a two-stage decomposition. The weight loss below about 487°C is the solid phase decomposition and the decomposition proceeds very slowly. The second stage starts at about 487°C and the decomposition proceeds rapidly until completion. The reaction product in the crucible is a monolith rather than loose powder, which indicates that melting occurred. Since the melting temperature of potassium chloride is higher than 700°C, only the perchlorate may melt. Therefore, the second stage is the liquid phase decomposition. In this case, the melting temperature of potassium perchlorate has been reduced substantially because of the formation of an eutectic between the perchlorate and the potassium chloride produced through the solid phase decomposition. It was reported that the mixtures of $KClO_4$ and KCl containing 30 and 50 mol% KCl start melting at 508 and 510°C respectively compared to the onset melting temperature of 570°C for $KClO_4$ alone [13]. It may be possible that an eutectic mixture with lower melting temperature is found in the composition range between 30 and 50 mol% potassium chloride.

4. Conclusions

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

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