Research Article
Coupling Effect of Metals and Oxides on the Oxygen Supply Performance of Sodium Chlorate Oxygen Candle

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In this study, to explore the influence of metals and oxides on the oxygen production rate and stability of sodium chlorate oxygen candles, 28 experimental samples were investigated. The effects of Co$_2$O$_3$, Co$_3$O$_4$, and Fe$_2$O$_3$ with different mass fractions on the thermal decomposition temperature and thermal decomposition rate of sodium chlorate were compared and analyzed. Co$_3$O$_4$ (5%) was obtained to reduce the thermal decomposition range to 260–450°C and reduce the pyrolysis interval $\Delta T$ to 46.2°C.

Through the development of three metals (Fe, Mg, and Mn), under four mass fractions (2%, 4%, 6%, and 8%) mixed with Co$_3$O$_4$ (5%), the results of the effective oxygen production efficiency test for the thermal decomposition reaction of sodium chlorate demonstrated that Mn (6%)–Co$_3$O$_4$ (5%) exhibited the best catalytic and heat coupling effect; the effective oxygen production efficiency of 97.8% was achieved. Oxygen candle oxygen supply experiment was conducted; the oxygen candle composition for the test was determined to be NaClO$_3$ (86%), Mn (6%), Co$_3$O$_4$ (5%), and kaolin (3%); in the four stages of the oxygen candle oxygen supply reaction test, the average oxygen supply rate reached 1.647 L/min, actual oxygen production was 28 L, and effective oxygen production rate of the oxygen candle was 53.6%. An increase of 9% was observed compared to the previous similar studies. The results of this study present a formula to optimize the oxygen supply of the oxygen candle, which is crucial for improving the oxygen supply performance of the oxygen candle.

1. Introduction

Oxygen candle, a solid oxygen source, possesses several advantages, such as high and fast oxygen production and large unit volume storage capacity; in addition, it has the advantages of unnecessity of additional power during use, stable usage volume, and easy to store and transport. Furthermore, the oxygen production and production rate of the oxygen candle are not affected by changes in the ambient temperature, humidity, and pressure [1–3]. Therefore, oxygen candles have been widely employed in aviation, submarine, mine rescue, and other fields [4].

Significant progress has been made in the research field of oxygen candles by various domestic and international researchers. Comparing the performance of common oxygen supply methods, Yajuan et al. analyzed the applicability of oxygen candles on plateaus [5]. Lei et al. analyzed the feasibility of the application of oxygen candles in deep-sea manned submersibles and proposed technical indicators suitable for emergency oxygen supply in deep-sea manned submersibles [6]. Shu et al. conducted a series of simulation tests and discussed the impact of oxygen candles on the living environment of a mining hazard space [7]. Shafirovich et al. used differential thermal analysis (DTA)/thermogravimetric analyzer (TGA) combined thermogravimetric analysis to conduct a binary thermogravimetric analysis of five common metals—Al, Fe, Co, Ni, and Sn—and NaClO$_3$; they investigated the catalytic effects of five metals on the...
thermal decomposition of NaClO₃ [8]. Gao and Liu [9, 10] optimized the oxygen production technology of the chlorate oxygen candle; in particular, they optimized the working principle, raw materials, and starting method [9] and studied the influence of manganese metal fuel on the pyrolysis of sodium chlorate oxygen candle [10].

The existing research results in this field are mainly to analyze the influence of single factor on the catalytic effect and technical index of oxygen candle. The coupling effect of metal and oxide on the oxygen supply performance of oxygen candles and the oxygen supply efficiency in closed space are lacking. Based on the previous research results and the oxygen production mechanism of NaClO₃ pyrolysis, the effects of oxides (Co₂O₃, Co₃O₄, and Fe₂O₃) and metals (Fe, Mg, and Mn) on the pyrolysis of NaClO₃ were compared and analyzed by thermogravimetric experiment. An optimized formula of oxygen candle with higher efficiency and better catalytic performance than the previous research was proposed, and the application effect of oxygen candle oxygen supply was verified by the oxygen candle oxygen supply test. The research conclusions provide a reference for improving the multifactor coupling oxygen supply performance of sodium chlorate oxygen candle.

2. Materials

2.1. Test Reagents and Instruments

2.1.1. Test Reagents. NaClO₃, analytically pure, Fe, Mg, and Mn were purchased from Beijing Tongguang Fine Chemical Co., Ltd. CO₂O₃ (99.9%), CO₃O₄ (99.9%), Fe₂O₃ (99.9%), and kaolin were purchased from Beijing Yihua Chengda Technology Co., Ltd. Silica aerogel felt insulation material was purchased from Zhongwei (Tianjin) Technology Co., Ltd.

2.1.2. Test Instruments. The test instruments include the constant temperature drying oven (DHG-9070A, Shanghai Jinghong Experimental Equipment Co., Ltd.), omni-directional planetary ball mill (QM-QX10, Nanjing University Instrument Factory), pressure testing machine (YES-300, Jinan Huaxing Experimental Equipment Co., Ltd.), thermal heavy mass spectrometer (STA449F3A-0660-M, Netzsch, Germany), and multifunction gas detector (Anpal Technology Co., Ltd.).

2.2. Experimental Methods

2.2.1. Sample Preparation

Thermal Decomposition Reaction. To avoid the influence of free water vapor in the medicine on the test, NaClO₃ was placed in a constant temperature drying oven at 80°C for 8 h before sample preparation; the sample proportioning was performed according to Table 1. We added 10 g of the proportioned sample to the ceramic crucible and manually stirred it for 10 min. A total of 28 samples were prepared.

Oxygen Candle Oxygen Supply Reaction. Based on the previous research results, the oxygen candle composition for the test was determined to be NaClO₃ (86%), Mn (6%), Co₃O₄ (5%), and kaolin (3%). The oxygen candle structure adopts a hollow structure, which promotes the reaction [11]. The composition, mass (Table 2), and size (inner diameter: 10 mm, outer diameter: 60 mm, and height: 64.5 mm) of the oxygen candle for the test can be calculated according to equations (1) and (2).

Theoretical Oxygen Supply of Oxygen Candle for Test. The absolute value of the maximum oxygen uptake of healthy adult men in China is 3.0 L/min–3.5 L/min; we assumed the uptake value as 3.5 L/min to prepare a sufficient amount of oxygen. Considering the influence of the volume of the oxygen candle during the oxygen supply test, to meet the 15 min oxygen demand of a healthy adult male, we determined an appropriate size for the oxygen candle during preparation. The oxygen demand calculation is as follows.

\[ V_{15\text{min}} = V_{\text{max}} \times t = 3.5 \times 15 = 52.5 L \]  

where \( V_{15\text{min}} \) is the 15 min oxygen demand of healthy adult men, \( V_{\text{max}} \) is the absolute value of the maximum oxygen uptake, and \( t \) is the maximum oxygen uptake time.

Composition and Quality of Oxygen Candle for Test. According to the main reaction equation of the oxygen candle production, the mass of the oxygen candle sample required to produce 52.5 L of oxygen was calculated, as given in Table 2.

Oxygen Candle Volume Size for Test. The density of the oxygen candle compressed by the oxygen candle selected in this test was in the range of 1.8 g/cm³–2.0 g/cm³, and the quality of the medicine required for the test was 318 g. According to equation (2), the volume of the oxygen candle required for an adult to breathe for 15 minutes was 176.7 cm³, inner diameter of the oxygen candle was 10 mm, outer diameter was 60 mm, and height was 64.5 mm.

\[ V_{\text{Oxygen}} = \frac{m}{\rho} \]  

where \( V_{\text{Oxygen}} \) is the volume of the oxygen candle sample, \( m \) is the mass of the oxygen candle sample, and \( \rho \) is the density of the oxygen candle sample.

We used an omni-directional planetary ball mill to grind and mix the sample for 5 min at a speed of 280 rpm and placed the ground oxygen candle sample into a self-made compression mold as shown in Figure 1. Subsequently, we used a pressure testing machine to pressurize the sample with a force of 35 KN. The oxygen candle body for the test was obtained from the mold [12], as shown in Figure 2.

2.2.2. Thermal Decomposition Reaction Test. We used Netzsch STA449F3A-0660-M thermogravimetric-mass spectrometry combined analysis equipment to perform thermal decomposition reaction tests on 28 samples. Herein, 15 ± 2 mg of each group of samples was weighed each time and placed in the thermogravimetric analyzer; subsequently, thermogravimetric analysis was conducted. The starting
temperature of the test was 25 ± 3°C, target temperature was 750°C, heating rate was 20°C/min, test gas was Ar, and flow rate was 40mL/min.

2.2.3. Oxygen Candle Reaction Experiment. Based on the previous research conclusions, the oxygen candle sample (86% NaClO3, 6% Mn, 5% Co3O4, and 3% kaolin) used in this experiment had an inner diameter of 10mm, an outer diameter of 60mm, and a height of 64.5mm. The weight of a single sample was 318g. The oxygen candle sample was placed in the reaction device, and silica aerogel felt was placed in the heat insulation structure as the heat insulation material; subsequently, this assembly was connected to the test instrument. The oxygen candle was placed in a closed box with a volume of 216 L, the remote ignition method was used to ignite it, and the Anpal multifunctional gas detector was used to monitor the gas concentration and oxygen production rate changes during the oxygen supply process of the oxygen candle. The gas detector data transmission module was used to output and analyze the experimental data as shown in Figure 3.

### Table 1: Proportioning table for the thermogravimetric experiment.

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### Table 2: Quality of the sample required for the experiment.

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<th>Mn</th>
<th>Co3O4</th>
<th>Kaolin</th>
<th>Total</th>
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<td>18.7</td>
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<td>318</td>
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</table>

3. Results and Discussion

3.1. NaClO3 Pyrolysis Reaction Analysis. The combined thermogravimetric experiment and 1# sample were used to analyze the thermal decomposition reaction process of pure NaClO3; the thermogravimetric (TG) curve obtained is shown in Figure 4 as a blank test. Pure NaClO3 began to decompose at approximately 520°C, TG curve began to decrease, and thermal decomposition reaction ended at approximately 600°C. The TG curve obtained was smooth, indicating that the pyrolysis process of pure NaClO3 is relatively stable. The main reaction equation is shown in the following equation [13, 14]. By comparing the process and regular pattern of the thermal decomposition reaction between the test sample and pure NaClO3, the effect of the catalyst and metal on the thermal decomposition reaction of NaClO3 was determined.

$$2\text{NaClO}_3 \xrightarrow{\Delta} 2\text{NaCl} + 3\text{O}_2 \quad (3)$$

The oxychloride anode comprises sodium oxychloride, metal fuel, oxide catalyst, and binder. Past research evidence shows that oxides can be catalysts, and the characteristic properties of metal oxide reactions form thermal reactions to provide energy. This study analyzed the effects of three oxides (Co2O3, Co3O4, and Fe2O3) and three metals (Fe, Mg, and Mn) on the thermal decomposition of NaClO3 [15].
Figure 5. The thermogravimetric curve of each sample is shown in Figure 6. Therefore, among the three metal oxides, Co3O4 (5-6%) has the best effect on accelerating the decomposition rate of NaClO3.

Three oxides of Co2O3, Co3O4, and Fe2O3 were selected as catalysts, and the mass fractions of each oxide were 2%, 3%, 4%, 5%, and 6%, and the 15 samples above are used to carry out the NaClO3 thermal decomposition reaction test. The thermogravimetric curve of each sample is shown in Figure 5. After adding the oxides (Co2O3, Co3O4, and Fe2O3) to NaClO3, the temperature ranges for the initiation and termination of the thermal decomposition reaction were 348–552°C (Co2O3), 260–450°C (Co3O4), and 366–558°C (Fe2O3), respectively. For the same oxide, the temperature range of the starting and ending reaction of the thermal decomposition reaction decreased with the increase in the oxide content. Among them, the oxide mass fractions of 5% and 6% did not significantly effect on the temperature and range of the thermal decomposition reaction. Therefore, Co3O4 is the best catalyst to control the temperature range of the thermal decomposition reaction.

3.2.3. Determination of High-Efficiency Oxide Catalyst Components. According to the analysis of the influence of oxides on the thermal decomposition reaction, it can be seen that among the three oxide catalysts, Co3O4 (5-6%) reduces the temperature range of the initiation and termination of the thermal decomposition reaction and has the best effect on accelerating the rate of thermal decomposition reaction. The corresponding T0.1 was 260°C, T0.9 was 306.2°C, and AT was 46.2°C; the catalytic effect did not change significantly within this range. Therefore, to increase the weight of NaClO3 in the thermal decomposition reaction mixture and ensure more oxygen generation, the Co3O4 (5%) was selected in this study.

3.3. Analyzing the Coupling Effect of Metal Oxide on Effective Oxygen Production Rate. Based on the previously reported studies [9–13], we selected four different proportions (2%, 3%, 4%, 5%), and 6% did not significantly effect on the temperature and range of the thermal decomposition reaction.
4%, 6%, and 8%) of three metals (Fe, Mg, and Mn) mixed with \( \text{Co}_3\text{O}_4 \) (5%) and analyzed the metal oxide effect on the thermal decomposition reaction of \( \text{NaClO}_3 \). The effective oxygen production efficiency of 17–28% (a total of 12) samples can be calculated as follows:

\[
\begin{align*}
N_{O_2} &= \frac{Q_{AO_2}}{Q_{TO_2}} \\
Q_{AO_2} &= TG \times \frac{m_0 \times V_{O_2}}{m_{O_2}} \\
Q_{TO_2} &= \frac{m_0 \times \omega_{\text{NaClO}_3}}{m_{\text{NaClO}_3}} \times \frac{3}{2} \times V_{O_2},
\end{align*}
\]

where \( N_{O_2} \) is the effective oxygen production efficiency, \( Q_{AO_2} \) is the actual oxygen production, \( Q_{TO_2} \) is the theoretical oxygen production, \( TG \) is the weight loss ratio of the sample, \( m_0 \) is the initial mass of the sample, \( V_{O_2} \) is the volume of 1 mol \( O_2 \) under standard conditions, which is \( 2.24 \times 10^4 \) mL, \( m_{O_2} \) is the mass of 1 mol of \( O_2 \) under the standard condition, which is \( 3.2 \times 10^4 \) mg, \( \text{NaClO}_3 \) is the mass fraction of \( \text{NaClO}_3 \) in the sample, and \( m_{\text{NaClO}_3} \) is the mass of 1 mol of \( \text{NaClO}_3 \) under the standard condition, which is \( 1.061 \times 10^5 \) mg.

Figure 7 shows that when single metal (2%, 4%, 6%, and 8%) is added, the corresponding effective oxygen production efficiency \( N_{O_2} \) of Fe (4%), Mg (8%), and Mn (6%) is higher, which is 96.5%, 97.2%, and 97.8%, respectively. For the same metal mass fraction, \( N_{O_2} \) of 2% (Mn), 4% (Fe), 6% (Mn), and 8% (Mg) is higher, which is 95.1%, 96.5%, 97.8%, and 97.2%, respectively. Among these, \( N_{O_2} \) of Mg (6%)–\( \text{Co}_3\text{O}_4 \) (5%) is the highest, which is 97.8%. Therefore, Mn (6%)–\( \text{Co}_3\text{O}_4 \) (5%) was selected as the metal fuel and catalyst of the oxygen candle body.

### 3.4. Experimental Analysis of the Oxygen Supply Reaction of Oxygen Candle

The oxygen supply reaction experiment can obtain the oxygen candle \( O_2 \) production rate curve.
Figure 8 and the oxygen candle O₂ concentration curve (Figure 9). The experiment was carried out for 53 min, and the entire oxygen supply reaction was divided into four stages: the initial reaction stage (0–6 min), rapid rise stage (6–13 min), rapid decline stage (13–17 min), and stable end-stage (17–53 min). In the initial reaction stage, the oxygen production rate in the reaction space was 0 L/min, and the oxygen concentration was maintained at 20%. This shows that the oxygen candle reacted slowly in the initial stage, and the gas monitoring system did not detect the generation of oxygen, and thus, the oxygen concentration in the reaction space did not change significantly. In the rapid rise stage, the oxygen production rate in the experimental space increased rapidly from 0 to 17.28 L/min, and the oxygen concentration reached the peak value of 50%, indicating that the rapid reaction at this stage resulted in a large amount of oxygen, and the gas monitoring system detected a large amount of oxygen around the oxygen candle. During the rapid decline stage, the oxygen production rate in the experimental space decreased rapidly from 17.28 to 0.5 L/min, and the oxygen concentration decreased to 33%. This shows that the oxygen supply reaction at this stage entered a slow stage, and the gas generated in the rapid ascent stage is gradually and evenly distributed in the test space; in addition, the oxygen concentration monitored by the gas monitoring system decreases gradually. At the stable end-stage, the oxygen production rate in the experimental space gradually tended to 0 L/min, and the oxygen concentration was maintained at 33%. This shows that the oxygen supply reaction of the oxygen candle at this stage is over, and the gas monitoring system shows that the space oxygen vacancy remains unchanged.
According to the following equations, the actual oxygen production of the oxygen candle oxygen supply device was 28 L, and the effective oxygen production rate was 53.6%.

\[ N_E = \frac{V_A}{V_T} \]  \hspace{1cm} (7)

\[ V_i = (C_s - C_i) \times V_b, \]  \hspace{1cm} (8)

where \( N_E \) is the effective oxygen production rate of the oxygen candle, \( V_A \) is the actual oxygen production of the oxygen candle, \( V_T \) is the theoretical oxygen production of the oxygen candle, which is 52.2 L, \( C_i \) is the oxygen concentration in the test space during the stable phase of the oxygen supply reaction of the oxygen candle, \( C_s \) is the oxygen concentration in the test space at the initial stage of the candle oxygen supply reaction, and \( V_b \) is the test space volume.

According to the following equation, the average oxygen production rate during the oxygen candle oxygen experiment was 1.647 L/min.

\[ \bar{v} = \frac{V_A}{T_A}, \]  \hspace{1cm} (9)

where \( \bar{v} \) is the average oxygen production rate in the oxygen candle oxygen experiment, and \( T_A \) is the reaction time of the oxygen candle in the oxygen candle oxygen experiment, which is 17 min.
Figure 7: NaClO$_3$–5% Co$_3$O$_4$ metal effective oxygen production efficiency curve.

Figure 8: Oxygen candle O$_2$ production rate curve of test space.

Figure 9: Oxygen candle O$_2$ concentration curve of test space.
4. Conclusion

(1) When the oxide catalysts (Co$_2$O$_3$, Co$_3$O$_4$, and Fe$_2$O$_3$) were added separately, the pyrolysis temperature of NaClO$_3$ reduced significantly, which decreased gradually with an increase in the mass fraction of the catalyst. When the mass fraction of the catalyst reached 4–6%, the pyrolysis temperature of NaClO$_3$ remains unchanged. The thermal decomposition temperature remained unchanged. The lowering effect of the three different oxides on the pyrolysis temperature of NaClO$_3$ was in the following order: Co$_3$O$_4$ > Co$_2$O$_3$ > Fe$_2$O$_3$. The order of pyrolysis rate was Co$_2$O$_3$ > Co$_3$O$_4$ > Fe$_2$O$_3$, and finally, Co$_3$O$_4$ (5%) was selected as the catalytic high-efficiency agent.

(2) When 2%, 4%, 6%, and 8% of metal (Fe, Mg, and Mn)-Co$_2$O$_4$ (5%) were added, the order of the effective oxygen production efficiency of Fe metal for NaClO$_3$ is Fe (4%) > Fe (6%) > Fe (2%) > Fe (8%), the order of the effective oxygen production efficiency of Mg metal for NaClO$_3$ is Mg (8%) > Mg (4%) > Mg (6%) > Mg (2%), the order of the effective oxygen production efficiency of Mn metal for NaClO$_3$ is Mn (6%) > Mn (8%) > Mn (4%) > Mn (2%), and the order of the effective oxygen production efficiency of different metals for NaClO$_3$ is Mn (6%) > Mg (8%) > Fe (4%). Finally, Mn (6%)-Co$_2$O$_4$ (5%) was selected as the metal fuel and catalyst of the oxygen candle body, with the highest oxygen production efficiency of 97.8%.

(3) Oxygen candle oxygen supply experiment showed that the optimized oxygen candle prescription (86% of NaClO$_3$, 6% of Mn, 5% of Co$_2$O$_4$, and 3% of kaolin) oxygen supply reaction is divided into four stages: initial reaction stage (0–6 min), rapid rise stage (6–13 min), rapid decline stage (13–17 min), and stable end-stage (17–53 min). The actual oxygen production was 28 L, average oxygen production rate was 1.647 L/min, and the effective oxygen production rate of the oxygen candle was 53.6%, which confirm an increase of 9% compared to that reported previously.

(4) Although the optimal ratio of oxygen candle and its actual oxygen supply efficiency are obtained through experiments, the specific equipment for oxygen supply by oxygen candle is not studied. In the future research, the basic theoretical research of oxygen supply by oxygen candle should be combined with the practical application equipment to realize the transformation of achievements.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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