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Study of a New Type of Fire Suppressant Powder of $Mg(OH)_2$ Modified by DOPO-VTS

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Abstract

A new type of fire suppressant powders of magnesium hydroxide ($Mg(OH)_2$) modified by DOPO-VTS has been manufactured. And the fire suppression effectiveness and physical-chemical properties were studied in this paper. Three kinds of powders were used to study their fire suppression efficiency through laboratory scale experiments in a confine space of 1*1*1m. The physical and chemical characteristics of pure $Mg(OH)_2$ and its modified powder were characterized by thermal gravity analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The results exhibited that these three kinds of powder were all high efficient for fire suppression and the modified $Mg(OH)_2$ powders by added 3% DOPO-VTS was more efficient than the $Mg(OH)_2$ powders added 1% DOPO-VTS and the origin powder. And the modified $Mg(OH)_2$ powder by added 3% DOPO-VTS could release the least CO and decrease the flame temperature sharply. Fire extinguishing and possible fire-suppression mechanisms have also been analyzed from three aspects: chemical inhibition, cooling effect and asphyxiation effect.

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Keywords: fire suppression, DOPO-VTS, $Mg(OH)_2$ powders, dry powder

1. Introduction

In order to protect environment and improve fire suppression effectiveness, it was significant to find a new kind of fire suppressants, especially after Montreal protocol was carried out in 2005. Many experimental and theoretical studies have been conducted in order to find new environment-friendly fire suppression agents and to improve the fire suppression effectiveness of powders. The previous research was more concerned on alkali salts and phosphate salts, and the methods of improving the fire suppression effectiveness were focused on three areas: decreasing powder particle size, powder modification and controlling the powder shapes [1-4].For example: A new kind of k-powder modified by silicone oil was produced by Kuang [4] which had a better dispersity and fire suppression effectiveness than common BC fire suppressants. A new kind of fire suppression powders was manufactured by Ni [5], which was a kind of $NaHCO_3$ powder covered by molecular sieve. The results showed that the new powders had better fire suppression effectiveness than the common BC $NaHCO_3$ powders.

However, finding new fire suppressants has already been significant and challenging. It was reported that $Mg(OH)_2$ powder was a kind of good fire suppressant for putting out fires and some fire suppression results were commented [6-8]. The fire suppression effectiveness and advantages of $Mg(OH)_2$ have been introduced and compared with the common BC and ABC commercial suppressants [6], and their detailed fire suppressant effectiveness were also studied. For example: fire

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suppression effectiveness of $Mg(OH)_2$ were described by Kuang [7] in a bench-test, compared to commercial BC powder, while the effectiveness were studied by wang, et al. [8], compared to ABC powders.

Though $Mg(OH)_2$ powder was a good fire suppressant, its fire suppression effectiveness could be still improved higher. The modification of powders was usually applied to improve the fire suppression effectiveness, so it would be also used in this paper. In recent years, the fire retardants have been dramatically improved; and more and more fire retardants have been used to improve the fire suppression effectiveness [9-10]. The 9,10- dihydro-9-oxygen mixed-10-phosphaphenanthrene-10-oxide (DOPO) [11-12] was a kind of phosphorus-based flame retardants with good fire retardant performance and its decomposed products were also environment-friendly and less poisonous. And the gas-phase decomposed products of DOPO and its corresponding ramification also had fire retardant effects [13-15]. DOPO-VTS was a kind of DOPO ramifications and it was often used to improve the extinguishing performance of $Mg(OH)_2$ powder. In the paper, $Mg(OH)_2$ powder was modified by DOPO-VTS and its extinguishing performance was discussed detailedly in order to study the influence on the fire suppression effectiveness of DOPO-VTS.

Thence, the physical-chemical properties and fire suppression effectiveness of $Mg(OH)_2$ powder modified by DOPO-VTS will be discussed in this paper.

2. Surface modification

2.1 Preparation of DOPO-VTS

(1) 0.2mol DOPO, 0.2mol Vinyl Trimethoxy Silane and 200ml benzene solvent were placed into a three-necked flask which was protected by Nitrogen, equipped with agitator arm, constant pressure funnel and reflux condensing tube.

(2) After the temperature reached 80℃ and DOPO got totally dissolved, 100ml benzene solvent with 0.2g AIBN was added into the three-necked flask and was agitated for 24 hours.

(3) Finally, the funnel was used to filtrate the non-reacted solid. And the solvent was removed by the method of distillation. The remaining colorless viscous liquid was the DOPO-VTS.

The detailed reaction process was as the following reaction:

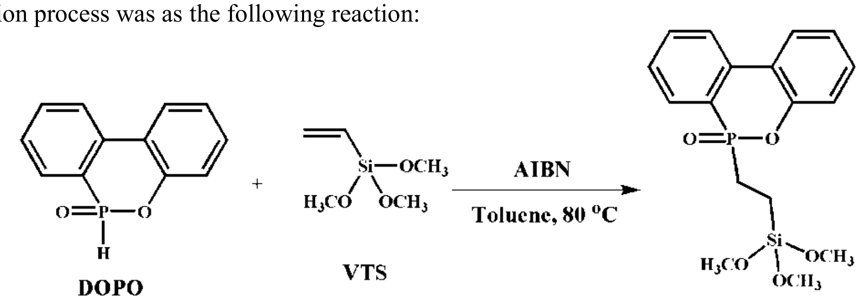

Fig. 1 Preparation process of DOPO-VTS

2.2 Preparation of modified $Mg(OH)_2$

(1)Firstly, 350g $Mg(OH)_2$, 3.5g DOPO-VTS, 500ml absolute ethyl alcohol and 50ml deionized water were placed into a 1000ml three-necked flask.

(2) Then, the temperature was rose to 80℃, and then the 70ml ammonia water (25%-28%) was added in the mixed liquor for a 6 hours reflux reaction.

(3) Finally, the reaction liquor was cooled to the ambient temperature and then the reaction liquor was suction filtrated by the vacuum filtrator. Afterwards, the filter cake was cleaned several times by deionized water and put into a 80℃dryer oven for 12 hours. The final residual solid was the modified $Mg(OH)_2$ powder.

(4) Repeating the method above, 3% DOPO-VTS was prepared by adding 10.5g DOPO-VTS in the 350g $Mg(OH)_2$ powder.

The detailed reaction process was as the following reaction:

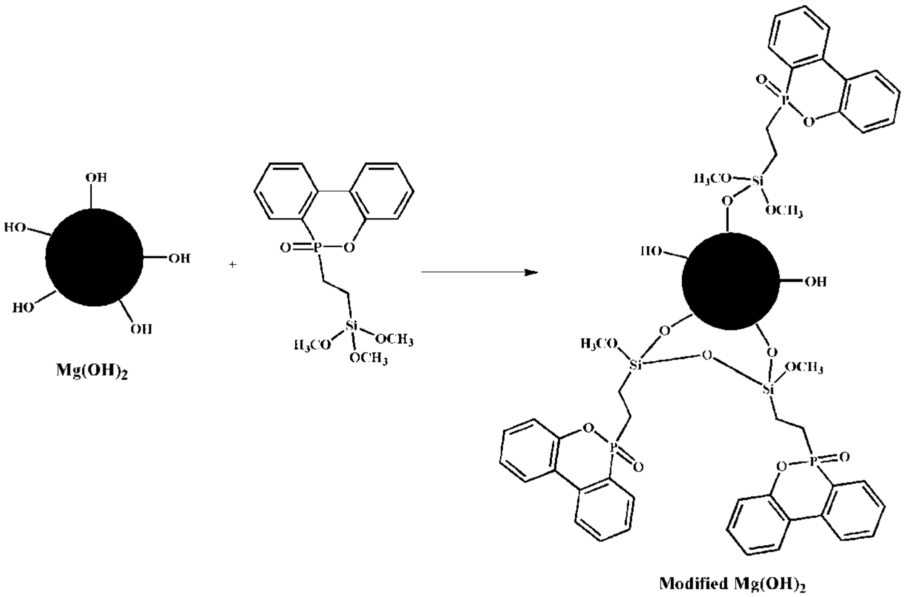

Fig. 2 Preparation process of modified $Mg(OH)_2$

3. Experiments

3.1 Experimental apparatus

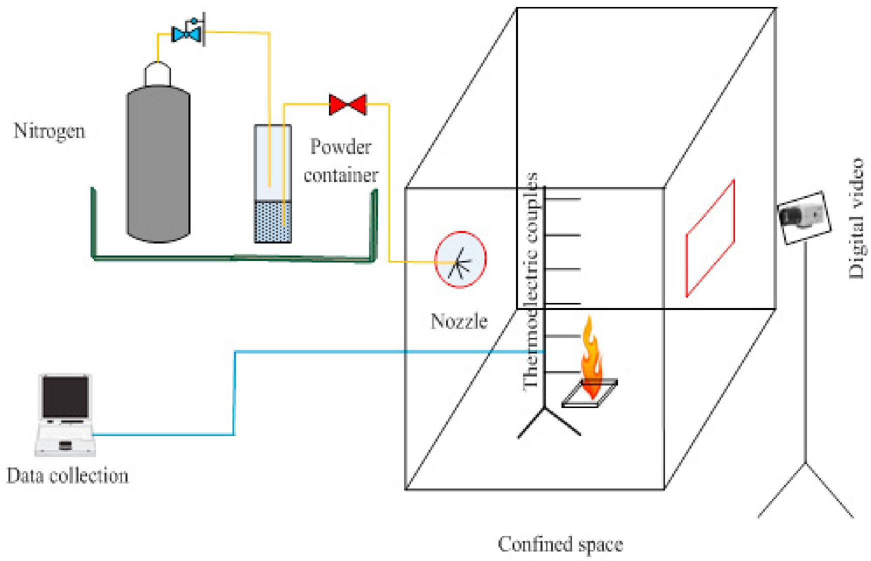

Fig. 3 Schematic of the experiment setup

The fuel was n-heptane and the oil pan was 10cm round pan. As shown in the Fig.3, the oil pan was set at the centre of the enclosed space. The flame temperature was recorded by 8 K-type thermocouples with 1mm diameter. 6 of them were distributed at the midperpendicular of the oil pan and the distance between them was 10cm. The distance between the first thermocouple and the bottom of the enclosed space was the same 10cm. The other 2 thermocouples were set at the place 4cm away from the central of the oil pan, which paralleled with the former 6 thermocouples to record the temperature of the boundary flame and the fuel. The powder nozzle was placed at the place 50cm away from central of the oil pan.

3.2 Experimental procedure

50g of the manufactured powder and 75ml n-heptane were poured into the powder container and oil pan, respectively. A certain pressure was adjusted as the driving force and then the fuel was ignited. After about 90s pre-ignition, the powders were sprayed out when the temperature kept stable. When the fire was extinguished, the ball valve was turned off immediately and then the measurement parameters of the whole process were recorded. The steps above would be repeated under different conditions and the data were also recorded.

4. Results and Discussions

4.1 TGA analysis of modified $Mg(OH)_2$ powder

The TGA parameters of $Mg(OH)_2$ powder was measured by TGA-Q5000 Thermogravimetric Analyzer under the air situation. The heating rate was 20℃/min, and the measure temperature ranged from 50℃ to 800℃. The detailed parameters were showed in Table 1.

Table 1 TGA parameters

parameters	mass, mg	Temperature rate,℃/min	Temperature range,℃
0	5.202	20	50~800
1% DOPO-VTS	4.394	20	50~800
3% DOPO-VTS	5.078	20	50~800

The Fig.4 showed that after adding the DOPO-VTS, the thermal stability of $Mg(OH)_2$ was improved at a certain extent. The complete decomposition temperature increased about 10℃, from 370℃ to 380℃. The TGA figure of two modified $Mg(OH)_2$ by adding 1% DOPO-VTS and 3% DOPO-VTS respectively were almost same. The Fig.5 showed that the modified $Mg(OH)_2$ by adding 3% DOPO-VTS reached its decomposition rate peak at a lower temperature than the other powders, that was, most of it decomposed at a lower temperature. The decomposition products of DOPO-VTS could suppress the combustion of fuel. Thus, it had a better extinguishing performance.

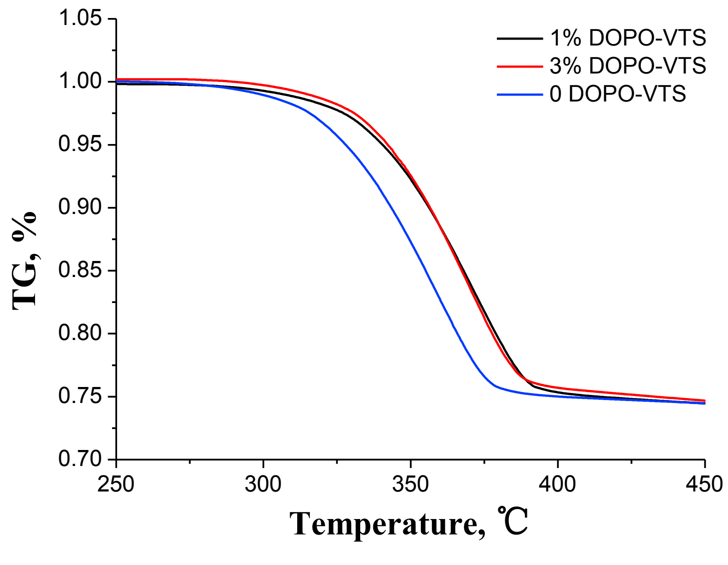

Fig. 4 TG results for the modified $Mg(OH)_2$ with DOPO-VTS

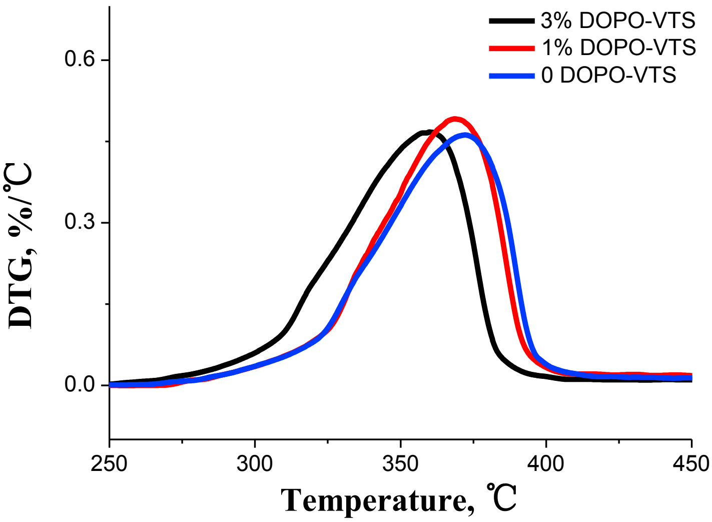

Fig. 5 DTG results of the modified Mg(OH)2 with DOPO-VTS

4.2 X-ray photoelectron spectroscopy (XPS)

The data was measured by thermo ESCALAB 250 XPS, the detailed parameter was showed in table 2.

Table 2 parameters of XPS

parameters	Source type	power	Spot size	Analyser Mode
	Al K Alpha	150W	500μm	CAE : Pass Energy 30.0 eV

As the following XPS figure, the chemical element of P and Si have been found, which indicated that the modification of $Mg(OH)_2$ powders is successful. And this new modified powder can be applied as a new kind of fire suppression powders.

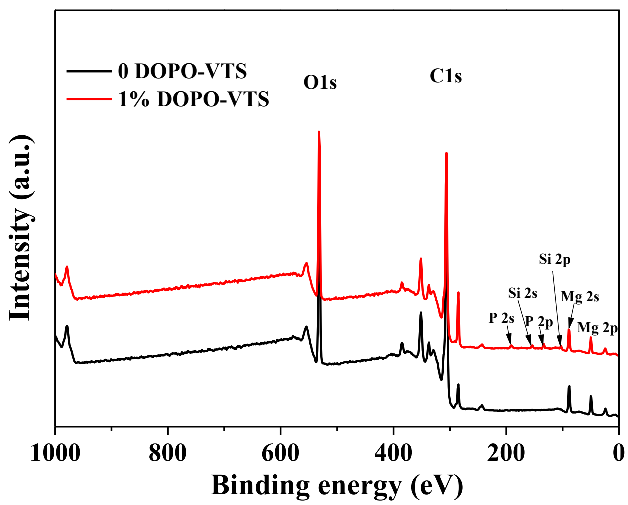

Fig. 6 XPS Spectrogram of modified Mg(OH)2 powders

4.3 Fire suppression time

The extinguishing performance of $Mg(OH)_2$ powder modified by DOPO-VTS was improved as shown in Fig.7. $Mg(OH)_2$ powder modified with 3% DOPO-VTS added had the best fire suppression effectiveness. That was mainly because that it reached the decomposition rate peak at a lower temperature. It released gaseous fire retardant more quickly which suppressed the spread of free radicals in the flame and finally put out the fire. What is more, the modified $Mg(OH)_2$ powder had better dispersion. Thence, it filled the whole space when it was sprayed in the 1×1×1m confine space and effectively made a 'powder wall' to decrease the radiation ability of flame and restrain the interaction between oxygen and the flame, which caused the fire to be extinguished.

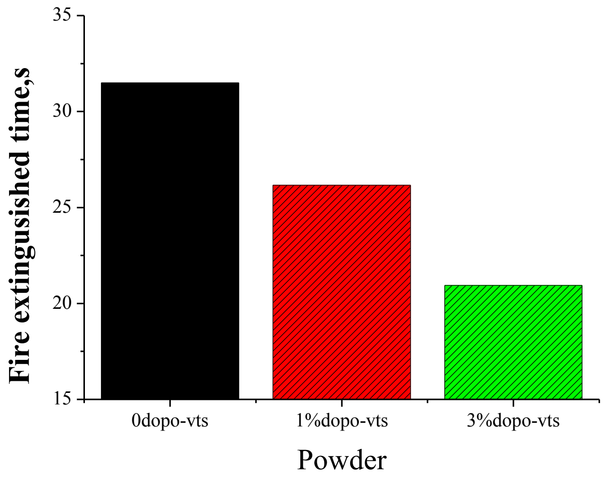

Fig. 7 Comparison of extinguishing performance of different modified powder

4.4 Fire suppression temperature

Fig.8 showed the flame temperature at the spot of 10cm away from the oil pan. Obviously, $Mg(OH)_2$ powder modified by adding 3% DOPO-VTS decreased the flame temperature the most rapidly and all these 3 kinds of powders finally put out the fire. $Mg(OH)_2$ powder modified by adding 1% DOPO-VTS put out the fire at a nearly same trend as the original $Mg(OH)_2$ powder did.

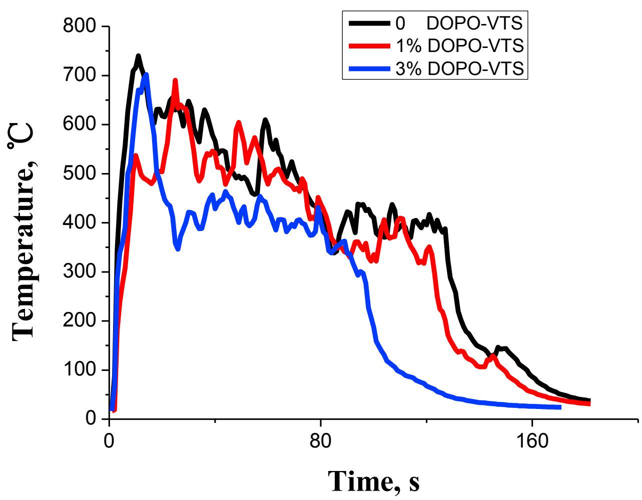

Fig. 8 Comparison of fire suppression temperature of 3 kinds of $Mg(OH)_2$ powder

4.5 Yield of CO

Fig.9 showed the CO concentration was affected by 3 kinds of powder. It showed that the peak of CO concentration of the modified $Mg(OH)_2$ powder by adding 3% DOPO-VTS was smaller than that of other 2 kinds of powder. Its decomposition rate was larger than that of other 2 kinds of powder, so it released the gaseous fire retardant within a shortest time, which could make the fire put out rapidly. Thence, the least CO was yield. The modified $Mg(OH)_2$ by adding 1% DOPO-VTS yielded a little lager CO concentration than that of origin $Mg(OH)_2$. This was because that after the DOPO-VTS decomposed, the yielded free radical could restrained the flame's complete combustion, when the fire the extinguishing times were nearly same.

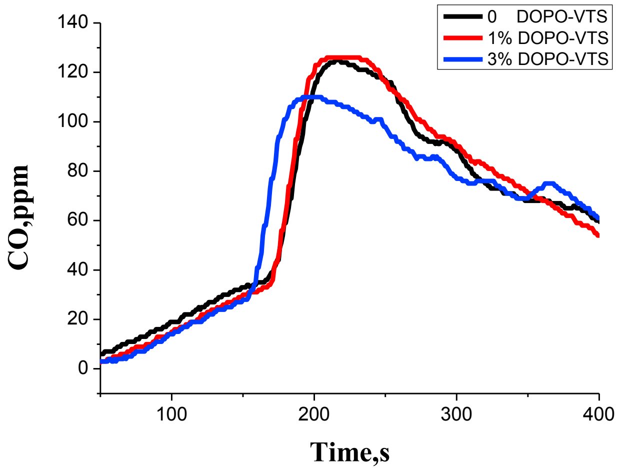

Fig. 9 The CO concentration affected by 3 kinds of powder

4.6 Fire suppression mechanisms

The fire suppression mechanisms of powder extinguishers have been mainly focused on 3 aspects: chemistry inhibition, cooling effect and suffocation effect.

(1)Chemistry inhibition

The •OH and H• were the key radicals to sustain fire in the chain reaction. When the magnesium hydroxide powders were sprayed into the flame region, the radicals would be absorbed or diluted and then the reaction chains were destroyed.

Combustion chain reactions could be broken by two modes: (a) powders reacted with the radicals, •OH and H•; (b) air flow dilutedthe radicals. Thence, during the decomposition process of the powder, 3 kinds of $Mg(OH)_2$ powders released certain particle absorbing the flame free radicals. And DOPO-VTS released gaseous phosphorous free radical which generated a stronger flame suppression effects.

The concrete reaction formula of DOPO-VTS reacting with the flame free radicals was showed as the following [16]:

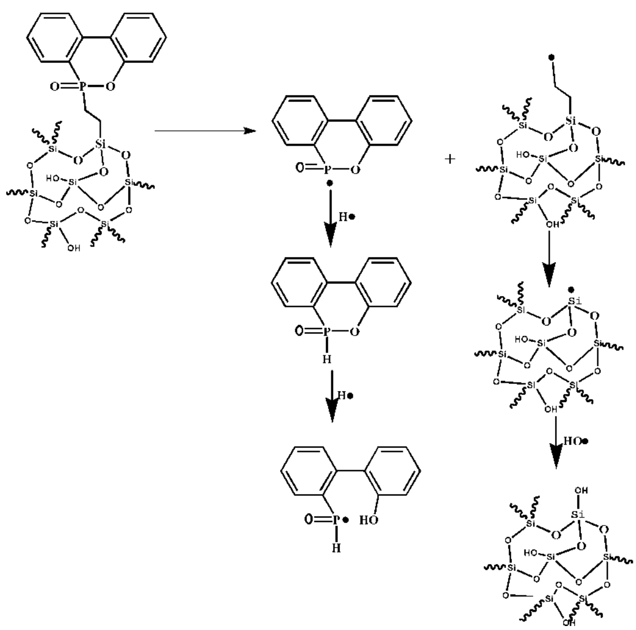

Fig. 10 Reaction mechanisms of DOPO-VTS with flame free radicals

Therefore, the reaction chains are destroyed further and finally the fires will be quenched.

(2)Cooling effect

The decomposition process of $Mg(OH)_2$ and DOPO-VTS required a large amount of heat, which decreased the flame temperature, and then kept the flame from continuous combustion. Compared to the absolute $Mg(OH)_2$, the modified $Mg(OH)_2$ needed more heat during the decomposition. At the aspect of the absorption of heat, the modified $Mg(OH)_2$ had better cooling effect.

(3)Asphyxiation effect

The modified $Mg(OH)_2$ had better dispersion performance. After the modified powders were sprayed out into the confine space, the space would be filled more quickly than $Mg(OH)_2$ powder and then a curtain or wall called 'black window' [17-18]was formed and the oxygen would be also isolated. The better dispersity was, the better isolated oxygen was. In addition, the better dispersion greatly increased the interaction chance between powder and flame, which still improved the powder's inhibition performance.

The added DOPO-VTS yielded the silicone dioxide which was heavier than the magnesium oxide yielded by $Mg(OH)_2$. So it could penetrate the flame, reach the fuel surface and cover it, which also improved the ability of isolation of oxygen and put out the fire more easily.

In a word, compared to the original $Mg(OH)_2$ powder, the fire suppression effectiveness of modified $Mg(OH)_2$ powder was better. However, for the 2 kinds of modified powder, their extinguishing performance depended on the volume of the additive, DOPO-VTS. In the work, the fire suppression effectiveness of the 3% DOPO-VTS added was better than the 1% added.

5 Conclusions

In the work, the fire suppression effectiveness of the pre-modified and the post-modified $Mg(OH)_2$ have been discussed respectively, the results were as follows:

(1)The $Mg(OH)_2$ powder modified by DOPO-VTS had a better heat stability. The start decomposition temperature and complete decomposition temperature was higher than that of the origin $Mg(OH)_2$. And the $Mg(OH)_2$ modified by 3% DOPO-VTS had a highest decomposition efficiency.

(2)The 3% DOPO-VTS-modified $Mg(OH)_2$ had a higher fire suppression efficiency than the 1% DOPO-VTS-modified $Mg(OH)_2$ and the origin $Mg(OH)_2$. The fire was put out quickly by all the 3 kinds of powder. The flame temperature was decreased sharply by $Mg(OH)_2$ powder modified by 3% DOPO-VTS.

(3) The CO concentration was affected by the 3 kinds of powder. The yielded CO concentration of 1% DOPO-VTS-modified $Mg(OH)_2$ was almost the same as the original $Mg(OH)_2$. However, the yielded CO concentration of $Mg(OH)_2$

modified by 3% DOPO-VTS was the least. It meant that the 3% DOPO-VTS-modified $Mg(OH)_2$ was more safe to people and was a good kind of new fire suppressants.

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