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Effects of Magnesium Hydroxide on Combustion Products of Polystyrene

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Pure polystyrene (PS) and PS composites containing magnesium hydroxide ($Mg(OH)_2$) were burned in a laboratory-scale combustion chamber. The analyses of combustion products were carried out by gas chromatography and gas chromatography/mass spectrometry. The results indicate that the effects of $Mg(OH)_2$ on combustion products of PS are obvious. With the increase of $Mg(OH)_2$, the concentration of CO_2 gradually reduces, and the majority of the volatile and semivolatile organic products, especially styrene monomer and some polycyclic compounds, take on increasing tendencies. Furthermore, the content of coke in residue also obviously increases because of the enhancement of $Mg(OH)_2$. All the changes seem to imply that the presence of $Mg(OH)_2$ alters reaction pathways during the combustion of PS, promotes incomplete combustion and decreases combustibility of PS.

Key words: Polystyrene, Magnesium hydroxide, Combustion products, GC/MS

I. INTRODUCTION

In the past decades, plastics have provided a fundamental contribution to all main daily activities: agriculture, furniture, automobile industry, electricity and electronics, architectural materials, packing, and so on. Due to their chemical constitution, plastics are very sensitive to flame. Therefore, the use of additives to improve their thermal stability is a widely-used way. So far, halogen-based flame retardants were widely used for this purpose, but the halogen-containing materials can cause the environmental and healthy problems because of the corrosiveness and the toxicity of their combustion products [1-3]. The work to find effective substitutes to replace them is an area of great interest. In this context, there is an increasing attention on inorganic compounds such as metallic hydroxide additives [4-6].

Magnesium hydroxide ($Mg(OH)_2$), as a halogen-free flame retardant, has come into widespread use to replace the traditional halogen-containing additives. Many investigations have concentrated on the use of $Mg(OH)_2$ as a flame retardant in thermoplastics [4-8]. Some studies have demonstrated that $Mg(OH)_2$ decomposes endothermically and releases water at about 300-320 °C, so that the flame retardant effect is based on cooling and dilution [4-6]. Even though a lot of work has showed that the existence of $Mg(OH)_2$ can improve the thermal stability of the thermoplastics, the flame retardant effects in the majority of researches were evaluated by the oxygen index, thermal gravimetric analysis and concalorimeter method.

In the present work, we investigated the changes of combustion products of polystyrene (PS) in the presence of $Mg(OH)_2$ with the aim to assess the fire-retarding effects of $Mg(OH)_2$ on PS from the aspect of combustion products.

II. EXPERIMENTS

A. Materials

PS (466F) was supplied by Yangzi-BASF Styrenics Co.Ltd.. $Mg(OH)_2$ with a median particle size of 1-2 μm was supplied by Anhui Huaxing Flame-retardant Co. Ltd.. PS and $Mg(OH)_2$ were dried at 110 °C for 2 h before use.

PS/20%$Mg(OH)_2$ and PS/30%$Mg(OH)_2$ composites were produced by mixing PS and the desired amounts of $Mg(OH)_2$ using a two-roll mill with a rotor speed of 64 r/min at a temperature of about 180-190 °C. After mixing, the samples were hot-pressed under 10 MPa to sheets of suitable thickness at about 180-190 °C for 10 min. Sample slabs of pure PS were also prepared by the same method.

Dichloromethane (CH_2Cl_2) and linalool used in the experiments were all analytical reagents. The results of gas chromatography/mass spectrometry (GC/MS) showed that there were no impurities in linalool, and three weak impurity peaks were observed in dichloromethane. The compounds identified from the impurity peaks were not considered during the qualitative analysis of combustion products.

B. Combustion procedures

Combustion experiments were conducted in a small-scale combustion system to obtain combustion products. The main part of the combustion system is a columniform chamber whose diameter and height are 6 and 30 cm, respectively. The combustibility of the

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sample can be observed through two parallel glass windows in middle part of the combustion chamber. A sample of three dimensions of 50 mm×6.5 mm×3 mm was fixed on a removable piston with screw thread under the combustion chamber. Air was passed through the combustion chamber from its bottom at the rate of 200 L/h. The schematic diagram of the combustion system is shown in Fig.1. Initially, K1 was turned on and K2 was turned off, and a ignited sample was extended quickly into the combustion chamber and the piston was tightened to guarantee the air tightness of the combustion system. Principal combustion products were expelled with air from the top of combustion chamber. Soot was headed off by a filter filled with stainless steel filament. Volatile and semivolatile organic products were collected by a Cambridge pad and downstream 30 mL of CH_2Cl_2. Before being vented to atmosphere, exhaust gas was treated with sodium hydroxide (NaOH) solution to avoid environmental pollution. At the end of the combustion process, the Cambridge pad was removed to a 100 mL conical flask and extracted with 50 mL of CH_2Cl_2 to dissolve the collected products. After being mechanically oscillated for 30 min, the CH_2Cl_2 extract was then filtrated. The CH_2Cl_2 solution collecting another part of volatile and semivolatile products was dried by anhydrous sodium sulfate and also filtrated. Whereafter, the two filtrates were incorporated and 0.1 mL of internal standard (0.693 g/L of linalool solution) was injected to the incorporated filtrate. Before GC/MS analysis, the incorporated filtrate was transferred into a K.D. concentrator and concentrated to 1 mL.
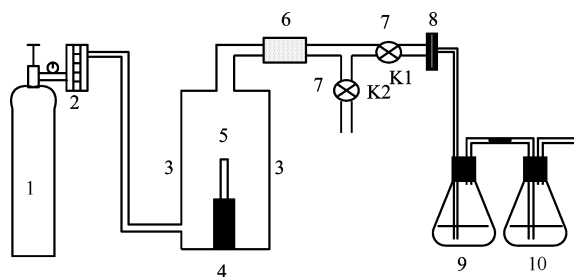

FIG. 1 The schematic diagram of the combustion system. 1. Air container; 2. Flow meter; 3. Glass windows; 4. Piston; 5. Sample slab; 6. Filter; 7. Valve; 8. Cambridge pad; 9. CH_2Cl_2; 10. NaOH solution

In addition, in order to acquire CO_2 gas, the above experimental procedure was reduplicated. Meanwhile, K1 was turned off and K2 was turned on, and the emitted gases were collected in a polyethylene bag.

C. Analysis of the products

CO_2 gas was analyzed in a GC-102 gas chromatograph (Shanghai Analysis Instrument Factory) equipped with a thermal conductivity detector (TCD). Chromatographic separation was performed on a 5A

molecular sieve column, hydrogen was used as the carrier gas and the GC oven temperature was set at 50 °C. The injection inlet temperature was 60 °C and the volume of injection was 1 mL. The CO_2 concentration was obtained by using 1 mL of CO_2 standard gas (99.99% minimum purity) as the external standard.

Analysis of the organic products was accomplished by a GC/MS instrument (Agilent Techn., Inc., 6890GC/5973MSD) using HP-5MS capillary column (30 m×0.25 mm×0.25 μm), with the following temperature programming: initial oven temperature was 40 °C, and held for 2 min; this was then raised to 250 °C at 4 °C/min and held for 10 min. Helium was used as carrier gas with a flow rate of 1.5 mL/min (constant flow). Programming temperature vaporizer (PTV) injector temperature was 250 °C, and the amount of injection was 1.0 μL at split mode (split ratio, 20:1). The temperature of the GC/MS transfer line was 280 °C. The MSD was operated in the electron impact (EI) mode. The ion source temperature was 230 °C and the electron energy was 70 eV. The mass range from m/z 35 to 500 was scanned.

III. RESULTS AND DISCUSSION

Samples were burned in a laboratory-scale combustion system. The reliability of the combustion system was proved by previous research [9]. The carbon dioxide in gas-phase products was measured by GC. For each sample, three replicate experiments were done and the corresponding experimental results were shown in Table I. As shown in Table I, the average concentration of CO_2 decreased from 2.00% for PS sample to 0.44% for PS/30%$Mg(OH)_2$ sample. It is obvious that the existence of $Mg(OH)_2$ leads to the termination of many intermediate reactions and incomplete combustion of PS.

TABLE I The concentration of CO_2 released from the combustion of three samples

Sample	Concentration of CO_2/%			
	Test 1	Test 2	Test 3	Average values
Pure PS	2.03	1.97	2.01	2.00
PS/20%$Mg(OH)_2$	0.59	0.66	0.57	0.61
PS/30%$Mg(OH)_2$	0.45	0.40	0.48	0.44

Combustion products collected by the CH_2Cl_2 and the Cambridge pad were analyzed with GC/MS. Figure 2 shows the total ion chromatograms of the combustion products of the PS/$Mg(OH)_2$ samples in comparison with that of the pure PS sample. The mass spectral identifications were carried out by comparing with the NIST02 mass spectral library as well as with the Wiley 275 L mass spectral library. Styrene trimer was identified by comparison with the spectra of authentic samples. Twenty seven main products and their yields acquired by the internal standard method were listed in Table II. On the whole, the products are mainly
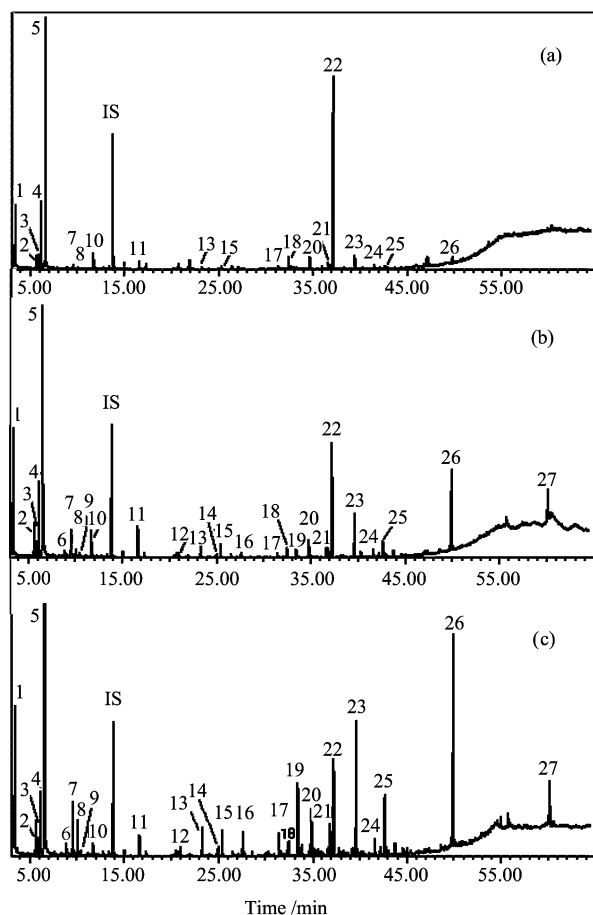
FIG. 2 Total ion chromatograms of the combustion products collected by the CH_2Cl_2 and the Cambridge pad ((a): PS; (b): PS/20%Mg(OH)$_2$; (c): PS/30%Mg(OH)$_2$; IS: internal standard peak).

hydrocarbons with benzene rings and can be classified into four groups according to the number of benzene rings: compounds having one benzene ring, two benzene rings, three benzene rings and four benzene rings. Moreover, some oxygenated compounds, such as benzaldehyde, benzofuran, phenol, isobutyl phthalate, and so on, were also found.

Figure 2 and Table II reveal that the presence of Mg(OH)$_2$ results in the formation of some new products. The results of quantitative analysis also show that the product distributions of the PS/Mg(OH)$_2$ samples are obvious different from that of the pure PS sample. With the increase of Mg(OH)$_2$, the majority of products, especially styrene monomer and some polycyclic compounds, take on increasing tendencies.

Moreover, the residues produced via the combustion of 1 g PS/20%Mg(OH)$_2$ sample and 1 g PS/30%Mg(OH)$_2$ sample in air atmosphere were measured. The yields of coke were calculated. The results are given in Table III. It can be seen from Table III that with the increase of Mg(OH)$_2$, the yields of coke obviously enhance. That is to say, the existence of Mg(OH)$_2$

promotes the formation of coke in the residue. All the changes seem to imply that the presence of Mg(OH)$_2$ alters reaction pathways during the combustion of PS.

Combustion of PS is a very complex process and when PS sample is combusted, there is generally a two-stage pyrolysis/combustion process [10-12]. First, PS is heated, releasing low molecular weight gaseous pyrolysis products followed by higher molecular weight gaseous products. This produces significant amounts of pyrolysates and forms a gas cloud of pyrolysis products around PS. Next, oxygen diffuses into the pyrolysis product cloud and a diffusion flame is established. Thus, some oxygenated compounds, such as CO_2, benzaldehyde, benzofuran, phenol, and isobutyl phthalate, were produced by oxidation reactions.

Rossi *et al.* have thought that the majority of products result from PS pyrolysis during the combustion of PS [13]. They are expelled from the reactor with airflow due to not oxidized in time. So, the effect of Mg(OH)$_2$ on pyrolysis zone is an important reason that induces the changes of these products. It is well known that the pyrolytic degradation of PS complies with a radical chain mechanism, including initiation, propagation, transfer and termination reactions [14,15]. Initiation reactions determine a C–C bond cleavage of polymer chains to form one primary radical (R$_1$) and one secondary benzyl radical (R$_2$). After the primary and secondary radicals are formed by scission of main chain, they can undergo continuous depolymerization to form a series of primary radicals and secondary radicals, and styrene monomer. Moreover, some of primary radicals and secondary radicals can also be transformed to the tertiary radical by intramolecular H-abstraction reactions because of their increased stability. This leads to the formation of styrene monomer, dimmer, trimer, and α-Methylstyrene via β-scission, as shown in Scheme 1.

Previous research showed that in certain temperature range, with temperature elevating, styrene monomer, dimer and trimer clearly reduce [16]. In the case of the PS/Mg(OH)$_2$ samples, when the reaction temperature exceeds 300 °C, Mg(OH)$_2$ dispersed in PS decomposes endothermically to water and magnesium oxide, and the associated endotherm is about 1.37 kJ/g [4-6], which leads to the falling of temperature in the pyrolysis zone. Therefore, with the increases of Mg(OH)$_2$, styrene monomer, dimer and trimer obviously increase.

During our experiment, some head-to-head structures as well as the same evolved products, such as toluene, ethylbenzene, biphenyl, diphenylmethane, bibenzyl, and 1,3-diphenylpropane, and so forth, were also found. The head-to-head structures as well as the same evolved products are likely to root in the composites of radicals such as R$_1$ and R$_2$ [14]. The radical composites can form the corresponding radicals by extensive random chain scissions, including the cleavage of C–C bond linking with phenyl rings to form phenyl radicals. The radicals formed through extensive random chain scissions can be then translated into the correspond-

TABLE II The combustion products collected by the CH_2Cl_2 and the Cambridge pad

Peak No.	t_R/min	Compounds	Similarity	Yields (μg/g)		
				Pure PS	PS/20%Mg(OH)$_2$	PS/30%Mg(OH)$_2$
1	3.43	Toluene	94	39.2	80.2	94.2
2	5.67	Ethylbenzene	94	9.1	23.9	26.3
3	5.92	*p*-Xylene	97	8.7	9.3	10.8
4	6.15	Phenylethyne	91	39.8	37.8	30.2
5	6.58	Styrene (monomer)	97	179.6	749.1	1105.3
6	8.86	Benzaldehyde	95	0.0	8.8	11.9
7	9.57	α-Methylstyrene	97	2.5	15.3	28.1
8	10.06	Benzofuran	95	2.8	3.4	3.7
9	10.20	Phenol	94	0.0	1.3	7.7
10	11.72	Indene	88	13.0	18.3	8.3
11	16.65	Naphthalene	91	5.5	18.7	11.9
12	21.02	1-Methylnaphthalene	91	0.0	2.7	5.4
13	23.30	Biphenyl	93	1.9	9.4	17.2
14	25.00	Diphenylmethane	94	0.0	2.0	6.7
15	25.41	Acenaphthylene	91	2.4	9.6	15.6
16	27.65	Bibenzyl	90	0.0	1.8	11.4
17	31.45	1,3-Diphenylpropane	95	2.0	3.1	12.6
18	32.47	9,10-Dihydroanthracene	92	7.5	6.0	9.1
19	33.32	2,4-Dipheny-1-butene (dimer)	90	0.0	6.6	37.0
20	34.78	Anthracene	93	10.1	10.5	24.8
21	36.87	1-Phenylnaphthalene	91	1.9	5.2	18.4
22	37.24	Isobutyl phthalate	90	123.9	64.2	44.1
23	39.62	2-Phenylnaphthalene	96	9.1	21.0	66.0
24	41.62	Fluoranthene	95	3.4	5.5	10.3
25	42.66	1-Benzylnaphthalene	86	1.5	8.5	34.2
26	49.91	2,4,6-Triphenyl-1-hexene (trimer)	–	3.8	49.4	125.6
27	60.13	1,3,5-Triphenylbenzene	99	0.0	30.3	45.5

Note: Styrene trimer was identified by comparison with the spectra of authentic samples.

TABLE III The Yields of residues and cokes after the combustion of two PS/Mg(OH)$_2$ samples

Samples	Yields of residue/%	Yields of coke/%
PS/20%Mg(OH)$_2$	16.7	2.9
PS/30%Mg(OH)$_2$	27.2	6.5

ing head-to-head structures as well as the same evolved products via intermolecular H-abstraction reactions or disproportionation reactions. Scheme 2 shows the possible formed pathway of 1,3-diphenylpropane [14]. The similar reaction fashion can account for the formation of other some head-to-head structures as well as the same evolved products. Their formed processes are simplified in Scheme 3.

Because of lower activation energy [17,18], radical recombination reactions are likely to become more important during the combustion of the PS/Mg(OH)$_2$ samples than during the combustion of the pure PS samples, which results in obvious enhancement of the head-to-head structures as well as the same evolved products.

On the other hand, magnesium oxide that is produced from the decomposition of Mg(OH)$_2$ forms metal oxide barrier layers to protect deeper layers of the material. Koverzanova *et al*. have explained the formation of more polycyclic compounds and coke during the oxidative degradation of polypropylene in the presence of Mg(OH)$_2$ by the catalysis of magnesium oxide [19]. The similar process maybe happens in the combustion of PS. Due to the weak basic properties and large active surface area, magnesium oxide causes dehydrogenation of PS accompanied by intramolecular and intermolecular cross-linking reactions. This promotes the formation of some polycyclic (hydrogen-deficient) products, such as anthracene, 1-phenylnaphthalene, 2-phenylnaphthalene, fluoranthene, 1-benzylnaphthalene and 1,3,5-triphenylbenzene, and so on, as shown in
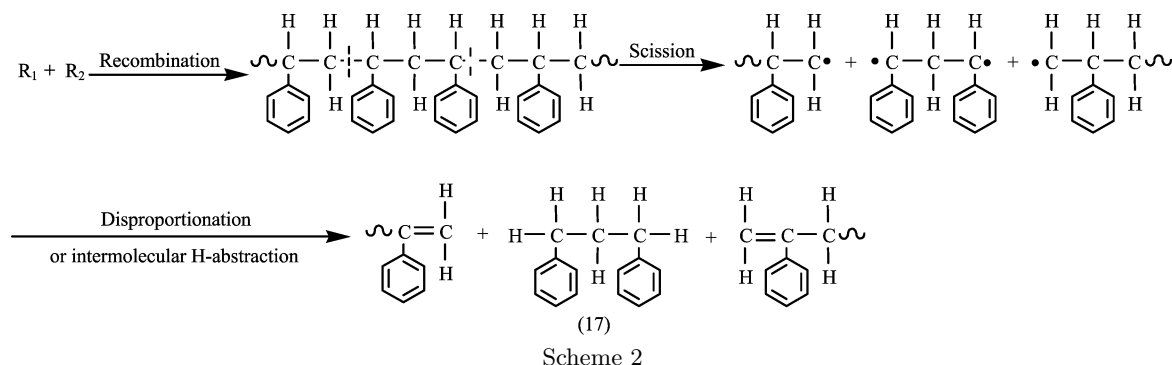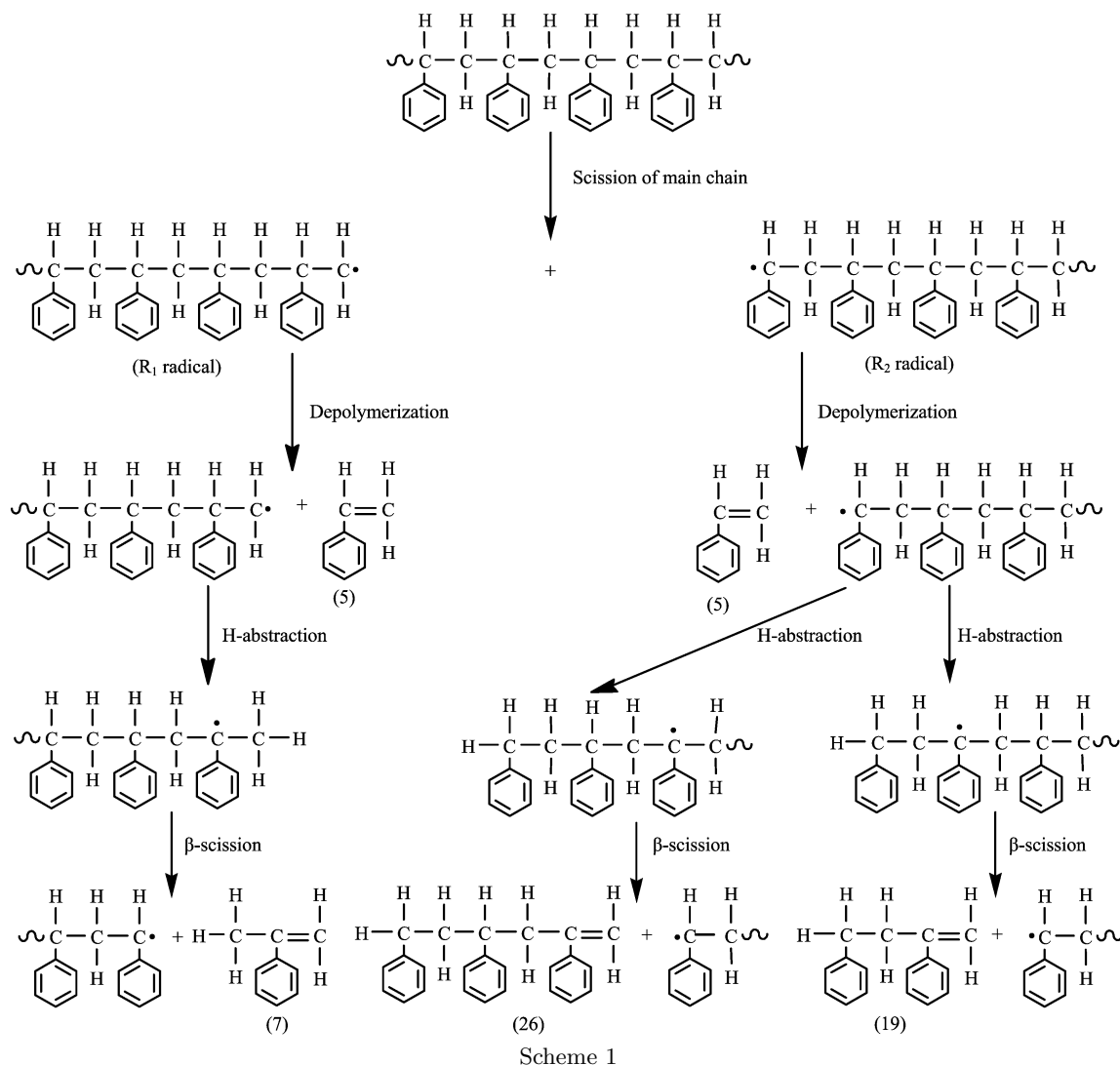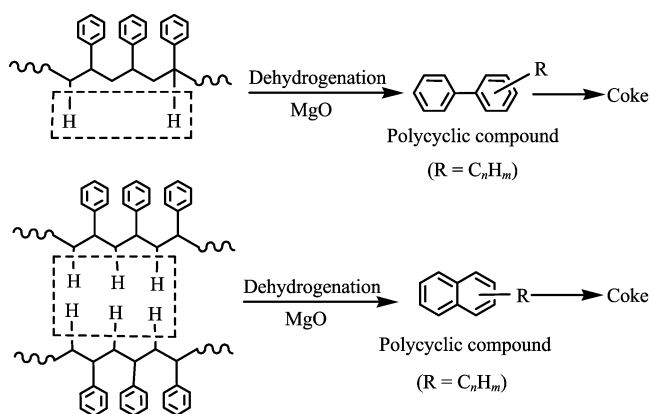
Scheme 1

Scheme 2

Scheme 4. Some researches have indicated that these polycyclic compounds are the precursors of some bigger polycyclic aromatic hydrocarbons and coke [20]. So, with the increase of these polycyclic compounds, coke residues also remarkably enhance.

Furthermore, the thermal and chemical balances in the combustion zone are also altered due to the existence of $Mg(OH)_2$ [21,22]. On the one hand, The water that releases from the decomposition of $Mg(OH)_2$ dilutes the amount of oxygen and the pyrolysis products available to sustain the combustion. On the other hand, the endothermal effect also reduces the temperature in the combustion zone. The diluent effect and the endothermal effect restrain the process of oxidation reactions and result in incomplete combustion. Therefore, principal oxygenated products, CO_2 and isobutyl
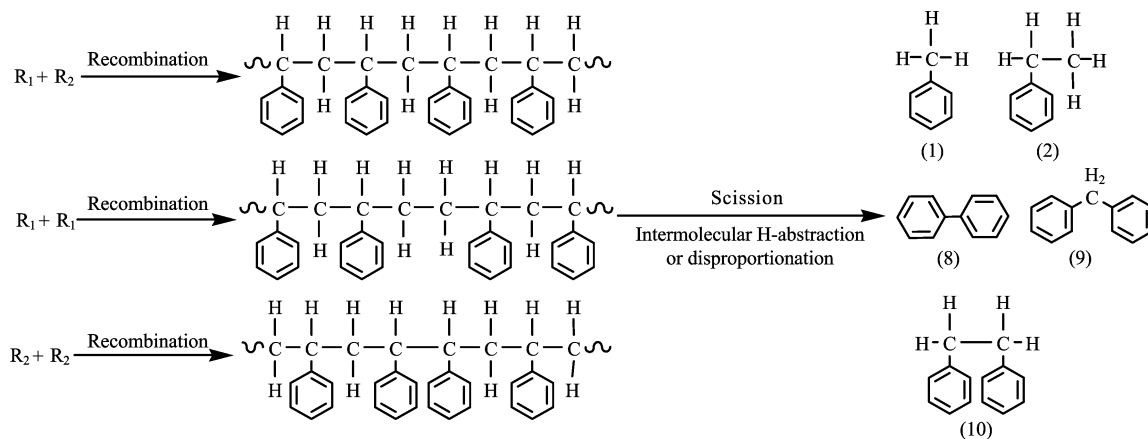
Scheme 3

Scheme 4

phthalate, clearly decrease because of the existence of $Mg(OH)_2$.

IV. CONCLUSION

The above research indicates that the effects of $Mg(OH)_2$ on combustion products of PS are obvious. The existence of $Mg(OH)_2$ results in the formation of some new products. The results of quantitative analysis also show that the product distributions of the $PS/Mg(OH)_2$ samples are obvious different from that of the pure PS sample. With the increase of $Mg(OH)_2$, the coke and the majority of the volatile and semivolatile organic products take on increasing tendencies and CO_2 markedly decreases. The changes hint that incorporation of $Mg(OH)_2$ into PS leads to changes of reaction pathways during the combustion of PS and promotes incomplete combustion. This demonstrates that this type of study is an effective method for understanding the fire-retarding effect and mechanism of $Mg(OH)_2$.

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