

Investigation on the thermal decomposition and flame retardancy of wood treated with a series of molybdates by TG–MS

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Abstract A flame-retardant wood was prepared using a series of insoluble molybdates through the double bath technique. The flame retardancy of the wood samples was studied with the limiting oxygen index (LOI) method. The relationships between the flame-retardant performance and the thermal property of wood were studied by the thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), scanning electron microscopy (SEM), and the thermogravimetry–mass spectrometry (TG–MS) analysis methods. The results showed that the insoluble molybdates, which were precipitated into the wood by the double bath technique, can obviously improve the flame retardancy of wood. Similarly, the transition metal molybdates showed higher flame-retardant efficiency than the main group metal molybdates do, which probably due to the thermal barrier effect that $\text{Fe}_2(\text{MoO}_4)_3$ acts during the combustion of the samples. At the same time, $\text{Fe}_2(\text{MoO}_4)_3$ catalyzed the dehydration and carbonization reactions of wood, and caused an increase in the amount of char produced, and an improvement of the stability of the char residue. Moreover, the mass spectrometry results indicated that the excess transition metal ions speed up the deep decomposition of the char residue, and resulting in the smoldering of wood.

Keywords Thermal degradation · Flame retardancy · Wood · Molybdates · Thermogravimetry–mass spectrometry

Introduction

For centuries, wood has been widely used both as structural and decorative material in buildings and for other uses. However, one of its key disadvantages is its high combustibility, which is determined by its composition [1–4]. The low-flammability of wood materials will contribute greatly to their applications, thus the study on flame-retardant treatment of wood materials aiming to improve the flame-retardant properties has attracted considerable industrial and scientific interests in recent years. Usually, the most common method to improve the flame retardancy of wood is chemical treatment with flame retardants [5].

The chemicals commonly used as flame retardants in wood include ammonium phosphate, phosphoric acid, boric acid, borax, hydrated aluminum, ammonia sulfate, zinc chloride, and magnesium chloride [6, 7]. Previous works have reported that the sodium molybdate can be used as an effective flame retardant for wood [8]. However, these chemicals are not suitable for exterior and underground construction, where the flame retardants are leached easily.

Now an important research orientation in flame retardants for wood is leaching resistant flame retardant. Commonly, they are applied in the use of the double bath technique. First, the material is impregnated with a soluble salt of the flame-retardant chemical in one bath, and then transferred it into another bath containing a precipitant. Lilla et al. [9] impregnated the wood with an aqueous solution of sodium silicate then with that of calcium chloride, they reacted and became insoluble hydrated calcium silicate in wood. Lipska

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et al. [10] suggested treating wood with the aqueous solution of diammonium hydrophosphate and the magnesium sulfate, and then, an insoluble ammonium magnesium sulfate would be obtained. Another good example is the case of precipitating mixture of oxides of tungsten and tin from their soluble salts [11]. Since these flame retardants can withstand washings in water, they have been classified as semi-durable finishes [11].

Although such systems have been examined in the previous studies, the optimization of the composition and the flame-retardant action of the flame retardants has not been completed. Moreover, no detailed quantitative information is available about the thermal decomposition products for wood treated with various molybdates. To complete the foregoing studies, thermal analysis and thermogravimetry–mass spectrometry analysis are employed to do the mechanism study.

Thermal analysis is a simple, convenient, fast and effective method for the study of pyrolysis and flame retardants [12–14]. The thermogravimetry–mass spectrometry analysis (TG–MS) is a very useful method to confirm the content and species of the gaseous products of the thermal decomposition, this method would be helpful to a better understanding of the actions of flame retardants and thus facilitating the development of new flame retardants.

In this article, the influence of series molybdates on the thermal degradation and flame retardancy of wood was discussed. The action of the flame retardants was also elucidated by the thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), TG–MS, and scanning electron microscopy analysis (SEM).

Experimental

Materials

Samples obtained from the sapwood portions of eugene poplar (Hebei Province, China) were used to determine the limiting oxygen index (LOI). The samples were 150 mm × 6 mm × 3 mm in size and were immersed in distilled water for 2 h at 90 °C, then thoroughly rinsed with distilled water and then oven-dried for 24 h at 70 °C.

FeCl₃·6H₂O, NiSO₄·7H₂O, CaCl₂, ZnSO₄·7H₂O, and Na₂MoO₄·2H₂O were purchased from Beijing Chemical-Reagents Corp., and each has a purity above 99.0%. Aqueous solutions of these reagents with concentration of 5 wt% were prepared.

Flame-retarding treatment of wood samples

Purified wood specimens at a size of 120 mm × 6 mm × 3 mm were immersed in FeCl₃·6H₂O, NiSO₄·7H₂O, CaCl₂,

and ZnSO₄·7H₂O aqueous solutions (5 wt%) at 80 °C for 2 h, and then oven-dried for 24 h at 70 °C. Then, put the dried samples into another aqueous solution (5 wt%) of Na₂MoO₄·2H₂O and standing for 2 h at 80 °C, and then oven-dried for 24 h at 70 °C. The samples were then stored in desiccators before being tested.

Leaching procedure

The leaching procedure in water was conducted according to the reference [15]. Five specimens per treatment were immersed in a 1,000 mL beaker containing about 400 mL distilled water (100-fold volume of specimens), and then the specimens were kept in the distilled water and stirred with a magnetic stirrer (300–400 rpm) at room temperature for a certain time, followed by drying at 70 °C for 16 h.

Mass percent gains (WG) of the flame-retardant specimens were calculated from the following equation:

$$\text{WG}\% = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where, W_0 is oven-dried mass (g) of a wood specimen before impregnation, and W_1 is the final oven-dried mass of the treated wood specimen with and without leaching procedure.

Limiting oxygen index (LOI) method

The LOI value is the minimum amount of oxygen in an oxygen–nitrogen mixture required to support combustion for more than 3 min, or until the specimen has been consumed by more than 5 cm from the top. LOI values were determined in accordance with ASTM D2863-2000 by means of a General Model HC-2 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China).

Thermal analysis

Thermal degradation of the samples was determined by TG, derivative thermogravimetry (DTG), and differential thermal analysis (DTA). The analyses were carried out on a WCT-2 thermoanalytical apparatus (Beijing Optical Instrument Co. Ltd., China). Samples weighing 7 ± 0.2 mg were placed in a platinum pan and heated from ambient temperature up to 800 °C at a rate of 20 °C min⁻¹ under air with a flow rate of 60 mL min⁻¹.

Scanning electron microscopy analysis

Firstly, the wood samples were placed in a muffle furnace in high pure nitrogen at 300 °C for 10 min, and then were cooled to ambient temperature. The morphology of the char formed in this way was investigated by means of a

SEM-KYKY-2800B SEM (Chinese Academic of Science Instrument Factory, Beijing, China). The surfaces of the char were coated with gold prior to analysis.

Thermogravimetry–mass spectrometry (TG–MS) analysis

A TG–MS instrument (STA 449 C-QMS 403 C, Netzsch Co. Ltd.) was used for analyzing fragments from the thermobalance. TG was performed in high purity argon (99.999%) at a flow rate of 25 mL min⁻¹. In the experiment, a sample weighing approximately 7 mg was heated at 10 °C min⁻¹ from ambient temperature up to 800 °C. Mass analysis was carried out using a spectrometer with an electron-impact ion source (70 eV); energy scanning was carried out in the range *m/z* from 10 to 160 at the rate of 0.2 s⁻¹ for each mass unit. The connection between the thermobalance and the mass spectrometer was done by means of a quartz capillary at 200 °C.

Results and discussion

Mass percent gains of wood samples and leachability of molybdates

As shown in Fig. 1, wood samples treated only with the soluble Na₂MoO₄ solution showed WG of 5.53%. For the double treatments, the WG values had obviously increased by treatment with the metallic salt solutions (5 wt%), four metallic salt solutions of Ca²⁺, Ni²⁺, Zn²⁺, and Fe³⁺ produce high WG values of 13.03, 12.02, 10.15, and 7.63%, respectively, suggesting the formation of inorganic substances in wood samples.

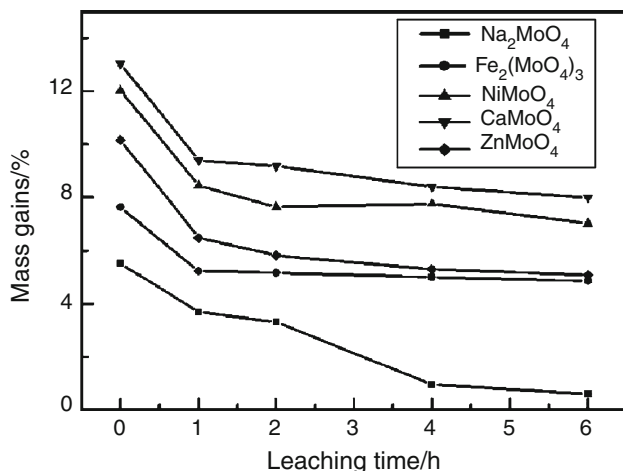


Fig. 1 Mass percent gains and leachability of molybdates from treated wood specimens

The results of the leaching tests of molybdates-treated woods are also shown in Fig. 1. It was found that calcium, nickel, zinc, and iron metamolybdates have slight solubility in water. The abrupt reduction of WG at the first hour of leaching means removal of unreacted chemicals; afterward, WG of chemicals decreased very slightly. However, the WG of Na₂MoO₄-treated wood samples decreased constantly with the increase of leaching time, and after 6 h of leaching, the WG of the sample is close to 0. These results indicate that the insoluble molybdate can be deposited in the wood by the double bath technique, which can prevent the flame retardants leaching from running water.

Flame retardancy of wood treated with various molybdates

The LOI results of both treated and untreated wood samples are listed in Table 1. From Table 1, it is evident that the LOI value of the samples treated with the four insoluble molybdates, CaMoO₄, NiMoO₄, Fe₂(MoO₄)₃, and ZnMoO₄, is much higher than that of the untreated sample and the Na₂MoO₄-treated sample. Moreover, the flame-retardant effects of insoluble molybdates show the following sequence: Fe₂(MoO₄)₃ > NiMoO₄ > ZnMoO₄ > CaMoO₄. In general, the transition metal molybdates are more effective than CaMoO₄.

Thermal analysis

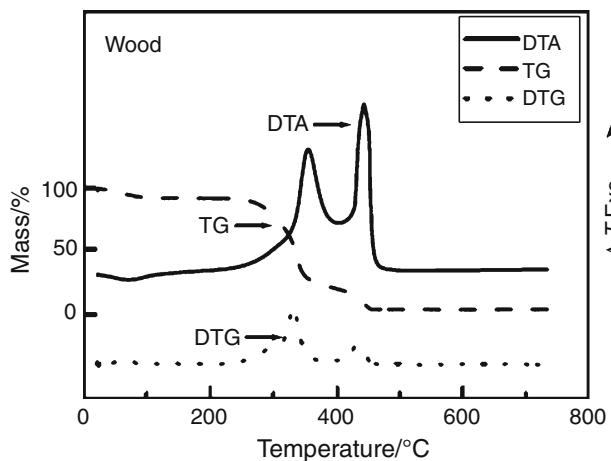
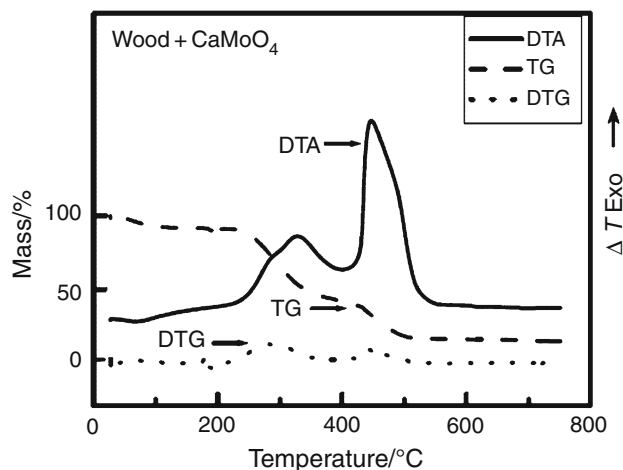
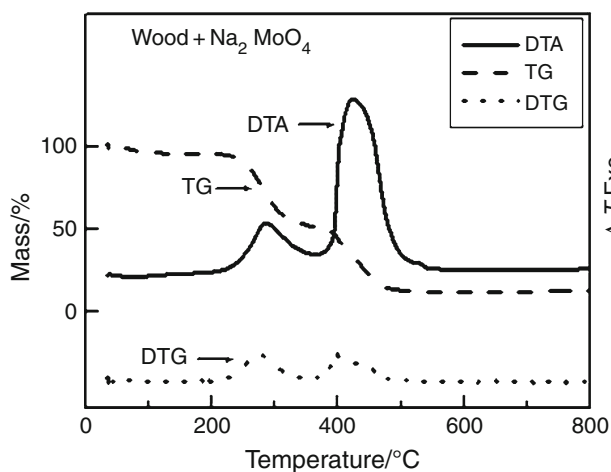
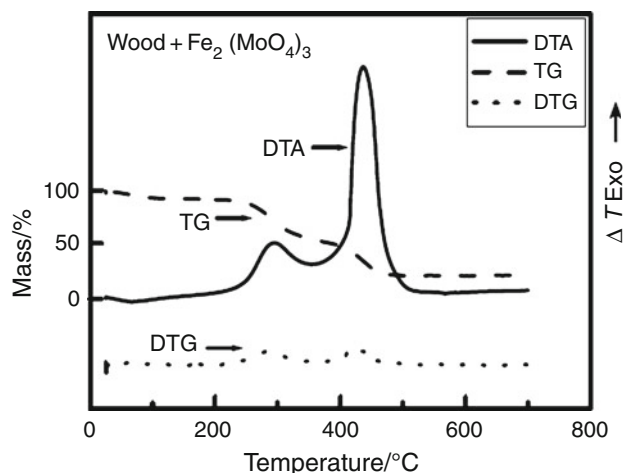
The representatives associated with TG, DTG, and DTA curves of the purified wood and for the samples treated with flame-retardant solutions are shown in Figs. 2, 3, 4, and 5. The related experiments were carried out in air from ambient temperature to 800 °C. From these figures, it can be seen that the TG and DTG curves of the thermal degradation process appear to be divided into three stages of mass loss: the drying stage, the charring stage, and the calcining stage [16].

As shown in Figs. 2, 3, 4, 5, and in Table 1, there is a mass loss in each sample at about 100 °C, which can be attributed to the removal of water from the wood. The charring stage, from approximately 220 to 350 °C, mainly involves the decomposition of hemicellulose and cellulose into char residues and the production of CO₂, CO, CH₄, CH₃OH, and CH₃COOH. During this stage, the mass loss on the TG curve accelerates gradually as the temperature is increased [16–18]. The calcining stage, from approximately 370 to 550 °C, mainly involves lignin decomposition and char residue oxidation [16–18].

At the charring stage, the TG results (Figs. 2, 3, 4, 5; Tables 1, 2) show that the process of degradation of the wood samples treated with flame retardants begins and

Table 1 the LOI and TG results of the samples

Samples	Charring stage			Calcining stage			Total mass loss/%	LOI/%
	$T_{\text{initial}}/^{\circ}\text{C}$	$T_{\text{final}}/^{\circ}\text{C}$	Mass loss/%	$T_{\text{initial}}/^{\circ}\text{C}$	$T_{\text{final}}/^{\circ}\text{C}$	Mass loss/%		
Wood	245.1	352.8	63.2	352.8	452.8	26.2	96.9	20.8
Na_2MoO_4	224.2	310.6	37.5	310.6	490.6	48.2	90.5	29.7
CaMoO_4	229.9	336.2	39.8	336.2	507.9	34.0	81.6	32.8
NiMoO_4	226.6	319.2	32.3	319.2	528.3	40.9	81.0	35.4
$\text{Fe}_2(\text{MoO}_4)_3$	233.9	326.6	32.6	326.6	477.2	40.4	81.0	36.6
ZnMoO_4	228.3	313.4	34.9	313.4	485.1	39.0	82.5	34.5

**Fig. 2** TG–DTG–DTA curves of the wood in air**Fig. 4** TG–DTG–DTA curves of the wood treated with CaMoO_4 in air**Fig. 3** TG–DTG–DTA curves of the wood treated with Na_2MoO_4 in air**Fig. 5** TG–DTG–DTA curves of the wood treated with $\text{Fe}_2(\text{MoO}_4)_3$ in air

reaches the maximum rate at lower temperatures than in the case of untreated wood. Compared with the untreated wood sample, the mass loss of the wood samples treated with flame retardants decreases by 23.4–30.9%, so the yield of the char residue increases. The flame retardants show a clear action of dehydration and carbonization.

Comparing the four insoluble molybdates-treated samples with the Na_2MoO_4 -treated ones, it is clear that the initial decomposition temperature (T_{initial}) and the final decomposition temperature (T_{final}) of the insoluble molybdates-treated samples are much higher than that of the Na_2MoO_4 -treated ones. For the CaMoO_4 -treated sample,

Table 2 DTG–DTA results of the samples

Samples	Charring stage		Calcining stage		$T_{E1}/^{\circ}\text{C}^e$	$T_{E2}/^{\circ}\text{C}^f$
	$T_{M1}/^{\circ}\text{C}^a$	$M_{w1}/\text{mg min}^{-1b}$	$T_{M2}/^{\circ}\text{C}^c$	$M_{w2}/\text{mg min}^{-1d}$		
Wood	331.6	3.267	431.7	1.138	354.7	443.2
Na_2MoO_4	272.2	0.885	394.5	0.953	285.6	423.9
CaMoO_4	280.3	0.879	431.6	0.756	327.8	446.4
NiMoO_4	276.5	0.832	421.0	0.719	296.0	437.7
$\text{Fe}_2(\text{MoO}_4)_3$	283.1	0.607	416.5	0.852	294.5	436.3
ZnMoO_4	268.5	0.852	413.8	0.963	286.5	434.2

^a T_{M1} the temperature of the maximum rate of mass loss in the charring stage

^b M_{w1} the maximum rate of mass loss in the charring stage

^c T_{M2} the temperature of the maximum rate of mass loss in the calcining stage

^d M_{w2} the maximum rate of mass loss in the calcining stage

^e T_{E1} the first exothermic peak temperature

^f T_{E2} the second exothermic peak temperature

although it shows the highest T_{final} , the mass loss of the sample at the calcining stage increases from 37.5 to 39.8%. These results indicate that the existence of Ca^{2+} would decrease the dehydration and carbonization of Na_2MoO_4 , and the enhancement of T_{initial} and T_{final} is merely because of the thermal barrier effect of CaMoO_4 to the wood, which is in accordance with the fact that the CaMoO_4 -treated sample shows a relatively high T_{initial} and T_{final} as well as the lowest mass loss rate at the calcining stage. As for the samples treated with the transition metal molybdates ($\text{Fe}_2(\text{MoO}_4)_3$, NiMoO_4 , and ZnMoO_4), although the enhancement of the T_{initial} at the charring stage is not as evident as the CaMoO_4 -treated ones, the mass loss of them is obviously lower than that of the samples treated with Na_2MoO_4 and CaMoO_4 , indicating that the transition metal molybdates not only act as thermal barrier but also reinforce the dehydration and carbonization of Na_2MoO_4 .

As shown in Table 2, the temperature of maximum mass loss rate (T_M) in both the charring stage and the calcining stage of the CaMoO_4 -treated sample is obviously increased compared with that of the Na_2MoO_4 -treated sample, but the maximum mass loss rate (M_w) in the charring stage of the CaMoO_4 -treated sample is only slightly decreased from 0.885 to 0.879 mg min^{-1} . These results reveal that the physical insulation effect of CaMoO_4 is less effective to improve the flame retardancy of the wood sample. Therefore, CaMoO_4 is the least effective flame retardants for wood among the insoluble molybdates. As for the Fe_2MoO_4 -treated sample, it shows not only a relatively high T_M in the charring stage but also the highest T_M (283.1 $^{\circ}\text{C}$) and the lowest mass loss rate (0.607 mg min^{-1}). These results indicate that it is the synergistic effect of the physical insulation and the dehydration that made $\text{Fe}_2(\text{MoO}_4)_3$ the

best flame retardant for wood among the insoluble molybdates. The latter point will be studied in the following.

What also can be seen from Figs. 2, 3, 4, 5, and Table 2 is that there are two exothermic peaks in the DTA curve of the wood samples. The first one is attributed to flaming combustion of volatile products; the second is attributed to glowing combustion of the char residual [2]. The DTA curve of the CaMoO_4 -treated sample is very similar to the DTA curve of the Na_2MoO_4 -treated sample, except that its first peak temperature (T_{E1}) and second peak temperature (T_{E2}) are obviously higher. All these facts indicate that as a thermal barrier, CaMoO_4 can hold back the heat transfer when the sample burns. However, the DTA curves of the samples treated with the transition metal molybdates are obviously different from that of the Na_2MoO_4 -treated ones. Especially for the DTA curves of $\text{Fe}_2(\text{MoO}_4)_3$ -treated and ZnMoO_4 -treated ones, their second exothermic peak changes to be more sharp and the T_{E2} increases obviously. These results show that the transition metal molybdates can catalyze the carbonization reaction of wood so as to generate more char residual at the charring stage, and thermal barrier effect would enhance the stability of the char residual at the calcining stage.

To verify the above conclusion, the morphology of the char residue was observed by SEM. As shown in Figs. 6, 7, and 8, the char residues of the treated and untreated wood samples are quite different. Compared with the untreated wood sample, it can be seen that it is gray color for untreated wood and black color for Na_2MoO_4 -treated sample. Moreover, there are some molten material can be observed on the surface of the char residue generated from the $\text{Fe}_2(\text{MoO}_4)_3$ -treated sample.

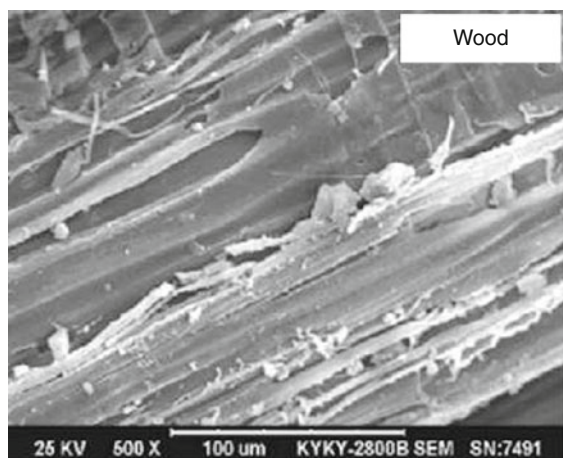


Fig. 6 SEM micrographs of the char (wood)

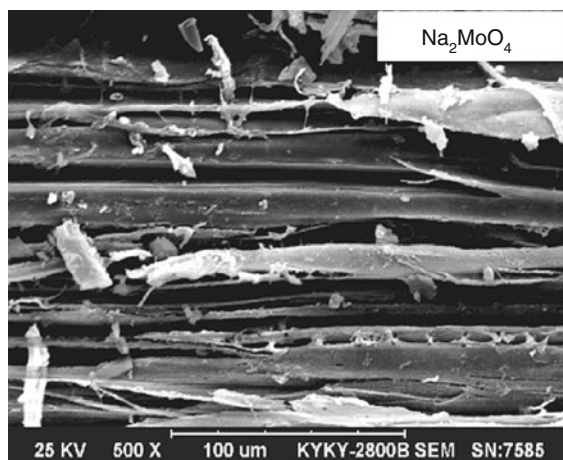


Fig. 7 SEM micrographs of the char (wood treated with CaMoO_4)

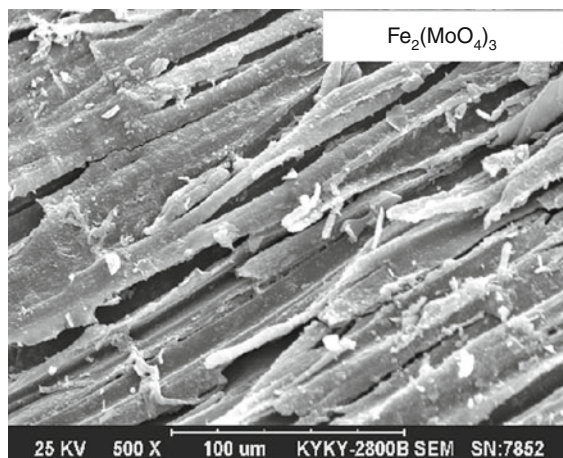


Fig. 8 SEM micrographs of the char (wood treated with $\text{Fe}_2(\text{MoO}_4)_3$)

TG–MS analysis

$\text{Fe}_2(\text{MoO}_4)_3$ has the highest flame-retardant efficiency for wood in the used molybdates, so we studied the flame-retardant mechanism of $\text{Fe}_2(\text{MoO}_4)_3$ and compared it with Na_2MoO_4 by TG–MS analysis.

TG of the wood sample was performed in argon, and the results (Figs. 9, 10) indicate only one degradation stage, from 220 to 400 °C. During this stage, the mass loss, the maximum mass loss rate, the T_{initial} , and the T_{M} of the treated samples decrease significantly compared to the untreated ones. This correlates to results of TG performed in air. Moreover, the TG curve of the $\text{Fe}_2(\text{MoO}_4)_3$ -treated sample is similar to that of the Na_2MoO_4 -treated ones, except that there will be an evident mass loss in the TG curve of the $\text{Fe}_2(\text{MoO}_4)_3$ -treated sample after 700 °C,

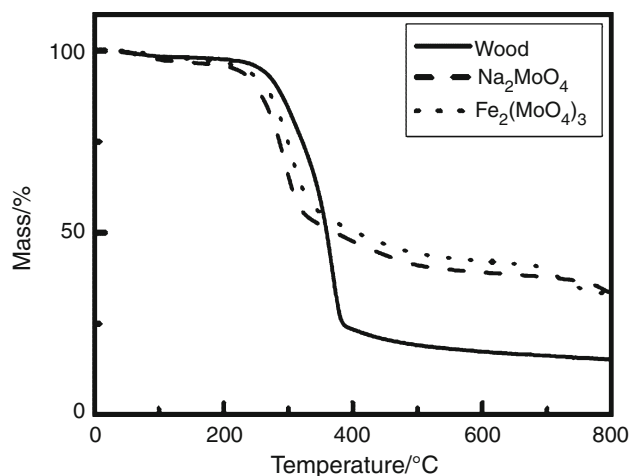


Fig. 9 TG curves of the samples (the samples were performed in argon, and the following rate is 25 mL min^{-1} , and were heated at $10 \text{ }^\circ\text{C min}^{-1}$)

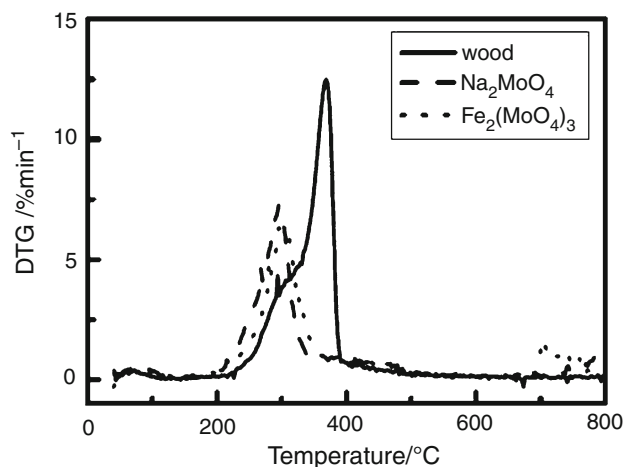


Fig. 10 DTG curves of the samples (the samples were performed in argon, and the following rate is 25 mL min^{-1} , and were heated at $10 \text{ }^\circ\text{C min}^{-1}$)

which indicates that $\text{Fe}_2(\text{MoO}_4)_3$ can promote the decomposition of the char residual at higher temperature, agreeing with the smoldering phenomenon that occurs when the $\text{Fe}_2(\text{MoO}_4)_3$ -treated wood sample burns.

Our previous work has reported that the sodium molybdate can be used as an effective flame retardant for wood [8]. It is clear that Na_2MoO_4 can effectively promote the intermolecular dehydration reaction and reduce the depolymerization reaction of wood, and these effects are contributed to the enhancement of the char residual yield. In order to further the study, the thermal degradation of the $\text{Fe}_2(\text{MoO}_4)_3$ -treated sample comparing with that of the Na_2MoO_4 -treated samples are studied by TG-MS.

As shown in Figs. 11, 12, 13, 14, and Table 3, the signals of $m/z = 12, 16, 18, 26, 28,$ and 44 MS samples are shown in ampere, respectively. Corresponding to the TG curves of the samples, all the ion peak signals of the flame-

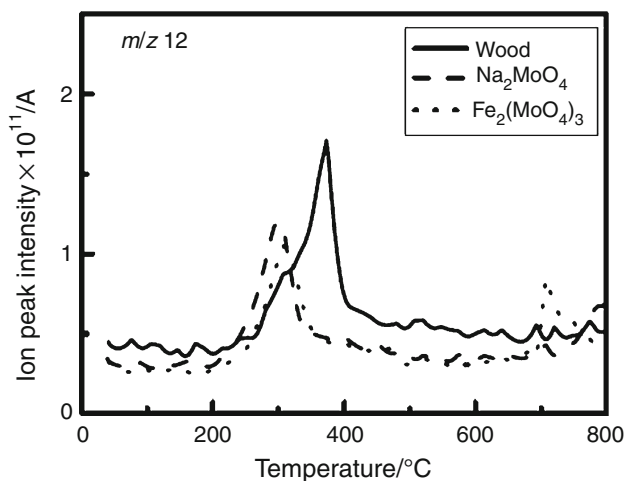


Fig. 11 MS results of the samples in argon (MS response of $m/z = 12$)

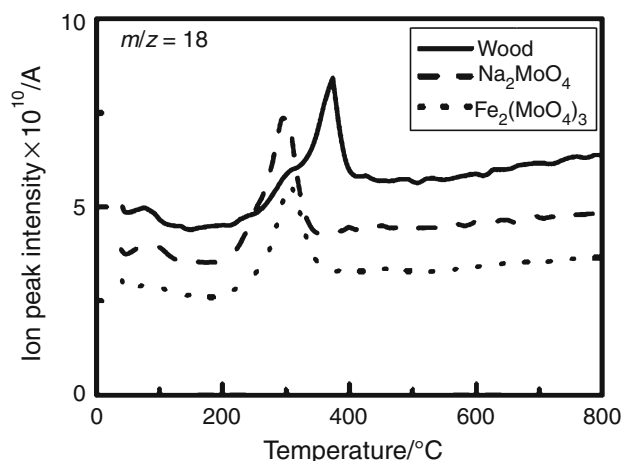


Fig. 12 MS results of the samples in argon (MS response of $m/z = 18$)

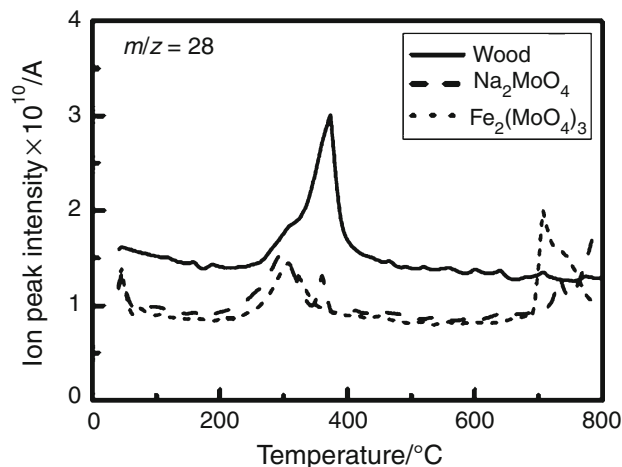


Fig. 13 MS results of the samples in argon (MS response of $m/z = 28$)

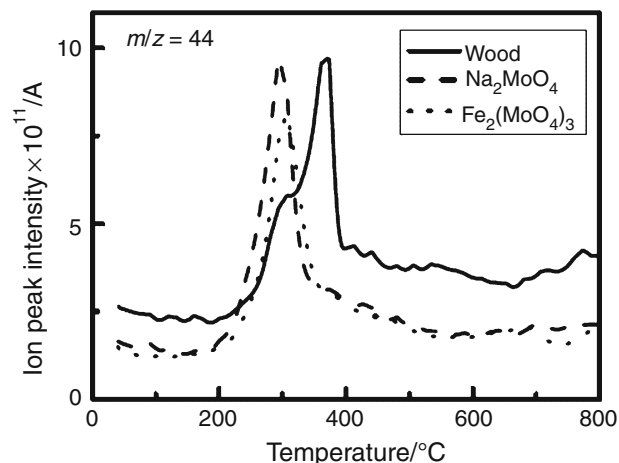


Fig. 14 MS results of the samples in argon (MS response of $m/z = 44$)

Table 3 TG-MS analysis results of the samples

m/z	Ion peak area $\times 10^9/\text{A s}$			MICI $\times 10^{11}/\text{A}^a$		
	Wood	Na_2MoO_4	$\text{Fe}_2(\text{MoO}_4)_3$	Wood	Na_2MoO_4	$\text{Fe}_2(\text{MoO}_4)_3$
12	5.20	3.95	4.06/1.14	1.71	1.18	1.05/0.84
16	11.27	9.42	8.68	5.74	4.89	4.08
18	96.85	117.08	94.15	84.5	73.6	56.14
26	3.50	1.14	0.75	1.39	0.48	0.46
28	50.09	26.89	22.36/28.01	30.1	15.5	14.49/20.00
29	27.00	6.59	6.43	8.24	2.02	1.91
30	9.92	2.58	2.51	2.86	0.84	0.76
44	29.52	34.16	30.27	9.70	9.8	8.14
60	0.72	0.13	0.085	0.27	0.16	0.15

^a MICI the maximum ion current intensity

retardant treated samples drop to a lower temperature about 70 °C. Compared with the Na₂MoO₄-treated sample, the Fe₂(MoO₄)₃-treated sample has resulted in the decrease of the maximum ion current intensity (MICI) and ion peak area of the MS signals (except for the ion peak area of the $m/z = 12$ MS signal), which indicates that the presence of the Fe₂(MoO₄)₃ leads to a lower evolution rate of the resulting fuel and/or to a different composition of this fuel. However, the ion peak area is not exactly reduced at the same tendency. For a detailed study of the changes in laws of the ion peak area, the reduction in the percentage of the ion peak area of the Na₂MoO₄-treated sample (R_{Na}) or the Fe₂(MoO₄)₃-treated sample (R_{Fe}) relative to the ion peak area of untreated sample were calculated with two formulas as follows:

$$R_{\text{Na}} = \frac{S_0 - S_{\text{Na}}}{S_0} \times 100\% \quad (1)$$

$$R_{\text{Fe}} = \frac{S_0 - S_{\text{Fe}}}{S_0} \times 100\% \quad (2)$$

where S_0 is the ion peak area of the untreated sample, S_{Na} is the ion peak area of the Na₂MoO₄-treated sample, S_{Fe} is the ion peak area of the Fe₂(MoO₄)₃-treated sample. The difference between the R_{Fe} and R_{Na} was also shown in Table 4 as $R_{\text{Fe}} - R_{\text{Na}}$.

As shown in Table 4, R_{Fe} of the fragment ions of $m/z = 16, 26, 28,$ and 60 are higher than R_{Na} , and $R_{\text{Fe}} - R_{\text{Na}}$ of the fragment ions of $m/z = 16, 26, 28,$ and 60 are 6.6, 11.1, 9.0, 6.2%, respectively. These results indicate that Fe₂(MoO₄)₃ can decrease the content of the fragment ions of $m/z = 16, 26, 28,$ and 60 in the gas phase. However, the total mass loss of the Fe₂(MoO₄)₃-treated sample is lower than that of the Na₂MoO₄-treated sample at about 8%, so the content of the fragment ions are decreased by Fe₂(MoO₄)₃, and it is mainly because of the dilution effect of Fe₂(MoO₄)₃. $R_{\text{Fe}} - R_{\text{Na}}$ of the fragment ions of $m/z = 29$ and 30 are lower than 1%, and R_{Na} of the fragment ions $m/z = 18$ (attributed to water [19, 20]) is a negative number, which means that Na₂MoO₄ can catalyze the dehydration of wood apparently. R_{Fe} of the fragment ions $m/z = 18$ is 2.8%, meaning that the output of water in the degradation progress of wood is decreased, and this is mainly due to the fact that the total mass loss of the Fe₂(MoO₄)₃-treated wood is lower at about 16% than the pure wood. Both R_{Na} and R_{Fe} of the fragment ions

$m/z = 44$ (which is mainly attributed to carbon dioxide [19, 20]) are negative numbers, which means that both Fe₂(MoO₄)₃ and Na₂MoO₄ can increase the output of carbon dioxide. These results indicate that Fe₂(MoO₄)₃ acts not only as thermal barrier to protect the virgin wood but also acts as a catalyst to increase the output of water and carbon dioxide.

$R_{\text{Fe}} - R_{\text{Na}}$ of $m/z = 12$ (which is attributed to ¹²C⁺) is a negative number, which means that there is more ¹²C⁺ in the gas phase of the Fe₂(MoO₄)₃-treated sample than the Na₂MoO₄-treated sample, and these results also can be seen in Table 3, the ion peak area ($m/z = 12$) of the Fe₂(MoO₄)₃-treated sample is higher than the Na₂MoO₄-treated sample (are 4.06 and 3.95, respectively). These results mean that Fe³⁺ can catalyze the degradation reaction of wood, so as to produce more char residual. However, in correspondence with the TG curve of the Fe₂(MoO₄)₃-treated sample, there is an ion peak ($m/z = 12$) after 700 °C and the ion peak area is 1.14 A s. What is more, there is an ion peak of $m/z = 28$ (which is mainly attributed to CO [19, 20]) after 700 °C, and the ion peak area is higher than the first ion peak in the charring stage. All these results indicate that Fe³⁺ has led to the depth pyrolysis of the char residual at the high-temperature, and the content of the incomplete oxidation products such as CO is increased, so Fe₂(MoO₄)₃ can arouse the smoldering of wood.

Conclusions

Insoluble molybdates can be precipitated into the wood by the double bath technique and then improve the flame retardancy of wood obviously. Among the insoluble molybdates, the transition metal molybdates show higher flame-retardant efficiency than the main group metal molybdates.

CaMoO₄ can increase the T_{initial} of wood significantly, but its presence can weaken Na₂MoO₄'s catalytic action to dehydration and carbonization when the wood sample burns. The main mechanism for CaMoO₄ to enhance the flame retardancy of wood is that CaMoO₄ acts as a thermal barrier and postpone the degradation of wood when the combustion happens. The transition metal molybdates such as Fe₂(MoO₄)₃, ZnMoO₄, and Na₂MoO₄ not only postpone the degradation of wood as a thermal barrier but also enhance Na₂MoO₄'s catalytic action to dehydration and carbonization of wood, causing the enhancement on decomposition temperature as well as the yield and stability of the char residual that generated at the charring stage. Moreover, the presence of Fe₂(MoO₄)₃ would enhance the output of water, carbon dioxide, and char residual and decrease the amount of flammable volatiles. However, Fe₂(MoO₄)₃ can cause deep pyrolysis of the char

Table 4 The reduction in the percentage of the ion peak area/%

m/z	16	26	28	60	29	30	18	44	12
R_{Na}	16.4	67.4	46.3	82.0	75.6	74.0	-20.9	-15.7	24.0
R_{Fe}	22.9	78.6	55.4	88.2	76.2	74.7	2.8	-2.5	21.9
$R_{\text{Fe}} - R_{\text{Na}}$	6.6	11.1	9.0	6.2	0.59	0.71	-	-	-2.1

residual at high temperature, as a result, the content of the incomplete oxidation products would increase so as to arouse smoldering of wood. Therefore, the amount of transition metal ions that are added into wood is worth further study.

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