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INFLUENCE OF SOME MINERALS ON THE CELLULOSE THERMAL DEGRADATION MECHANISMS

Thermogravimetic and pyrolysis-mass spectrometry studies

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The influence of different inorganic salts ($MgCl_2$, $ZnCl_2$, $NiCl_2$ and H_2PtCl_6) on the primary mechanisms of cellulose thermal degradation has been conducted by using thermogravimetric (TG-DTG) and pyrolysis-mass spectrometry (Py-MS) analysis at low heating rate (10°C min^{-1}) from ambient temperature to 500°C. The results clearly demonstrate that the used salts influence the primary degradation mechanisms. Furthermore, we can assume that some inorganic salts could be considered as specific catalysts and some others as inhibitors. $MgCl_2$ promotes selectively initial low temperature dehydration as observed both by TG and Py-MS. $ZnCl_2$ strongly changes the thermal behaviour of impregnated sample. The maximum mass loss rate temperature is shifted to lower temperature and on the basis of our results we can conclude that $ZnCl_2$ acts as catalyst in all primary degradation mechanisms. $NiCl_2$ and H_2PtCl_6 do not modify significantly the cellulose thermal behaviour but change the composition of both produced gases and liquids suggesting that these minerals catalyse some secondary reactions.

Keywords: *catalysis, cellulose, low heating rate pyrolysis, Py-MS, thermal degradation*

Introduction

It has now been confirmed that biomass pyrolysis is a viable route for producing gases and liquids that can replace some petroleum-derived products. Furthermore the possibility of obtaining useful chemicals has also been demonstrated [1]. The biorefinery concept producing the raw materials needed by the chemical industry on the basis of biomass has been proposed recently [2]. The interest is the widespread biomass availability as renewable source and his low impact on green house effect. It is commonly agreed that cellulose, which is the most frequent and generally the most abundant biomass component, can be considered as a model for biomass. Such an assumption is not fully satisfactory, both because cellulose is only partially representative of biomass and is not a precisely defined chemical species, given that its properties depend notably on the polymerization degree and the production process [3]. In any case, because of the complexity of biomass pyrolysis, data obtained on cellulose represent a good starting point.

The cellulose thermal decomposition has been studied intensely for many years [4–8]. Fundamental and applied studies of cellulose pyrolysis have attempted to elucidate the decomposition pathways, product distributions and chemical kinetics. When cellulose is heated under an inert atmosphere, it undergoes various dehydration, fragmentation, elimination and condensation reactions to give a plethora of gaseous products, a complex semi-volatile liquid tar and a residual carbonaceous char. The fractions distribution is strongly depending on the temperature and the heating rate. Schematically, the higher the temperature and the heating rate, the higher the amounts of gases. Reciprocally, the lower the temperature and heating rate, the higher the solid production [9, 10].

Despite considerable researches, there is still extensive debate on the global pyrolysis mechanism for cellulose. According to Grønli and Melaaen [11], kinetic modelling is very complicated and after nearly 30 years of research there is nowadays no consensus concerning the kinetics of wood (and cellulose) pyrolysis. The classic cellulose model, proposed by Broido-Shafizadeh, has for some time been considered as standard [12, 13]. Several studies throw doubt on the validity of the classic model [14, 15] and especially an important point concerns the generalisation of reactional schemes for a large domain of heating rate (from 1°C min^{-1} to fast pyrolysis) [16].

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The effect of metal ions addition on cellulose pyrolysis and on the volatile and non-volatile distribution products has been reported in several publications [17–25]. Major of these investigations had quite different fields of interest: works dedicated to the general interest in mechanistical and kinetical aspects of this pyrolysis reaction [17, 18, 22, 23], experiments focusing on the selective increase in yield for a specific pyrolysis product after the addition of salts [19, 25] but also investigations coming from the fields of fire prevention [26, 27]. Furthermore, it was found that certain minerals (such as Ca, K, Na, Mg and Fe) have a significant catalytic effect and even a small amount of them is sufficient to alter pyrolysis behaviour to a large extent. Previous researches have revealed the catalytic effect of mineral matter on biomass pyrolysis through various methods, such as demineralization (water or acid washing) or mineral addition in biomass [20, 28–32]. Recently, it was demonstrated for example that the pyrolysis of metal impregnated biomass by Fe and Ni salts is an innovative way to produce gas fuel [33].

In this work, several metallic cations (Mg^{2+}, Zn^{2+}, Ni^{2+} and Pt^{4+}) were chosen to investigate the cellulose pyrolysis and focused on their effects on primary reactions of thermal degradation. Mg^{2+} is one of the most abundant metal in biomass and is representative of alkali metals [34]. Ni^{2+} and Zn^{2+} represent the transition metal family. Ni^{2+} is widely used in pyrolysis/gasification process for reforming tar [35] and Zn^{2+} has a well known effect in biomass degradation for changing the liquids and gaseous yields [36]. Platinum is used as a representative of the noble metals. The purpose of this paper is to apply the technique of TG and Py-MS analysis to evaluate the influence of selected minerals on the impregnated cellulose thermal degradation. More specifically, the authors investigate the pyrolysis of the samples from ambient temperature up to 500°C at low heating rate (10°C min^{-1}) and the evolution of some representative primary degradation products is discussed.

Experimental

Sample preparation

Commercial cellulose (Microgranular cellulose-Sigma Aldrich) was impregnated with Ni(II) chloride hexahydrate 99% (Aldrich), Mg(II) chloride hexahydrate 99% (Merck), Zn(II) chloride hexahydrate 99% (Prolabo) and Pt(IV) chloride hexahydrate 40% (Merck). Cellulose (5 g) was impregnated by the different chloride salts using 50 mg solution of metallic cations (1% mass in respect to the cellulose amount) dissolved in 30 mL of distilled water. The mixture was gentle stirred at 75°C during 7 h and then dried at 100°C for 12 h.

Methods

Thermogravimetric analysis (TG-DTG)

Pyrolysis of pure and impregnated cellulose samples was performed in a thermogravimetric analyzer (Setaram TGA92). The sample (~30 mg) was first heated at 10°C min^{-1} to 95°C from the ambient temperature and kept isothermal for 15 min to remove moisture. Then it was heated up to 500°C at 10°C min^{-1}. The flow rate of carrier gas (Argon) was kept at 60 mL min^{-1}.

Pyrolysis-mass spectrometry (Py-MS)

Py-MS experiments were performed in a Pyroprobe 2000 pyrolyser interfaced to a gas chromatograph (Agilent 6890) with a mass selective detector (Agilent 5973) using an empty column (Fused Silica Kapillars, 10 m×0.25 mm). The sample (5–8 mg) was placed into a quartz tube and pyrolysed from 25 to 500°C at a heating rate of 10°C min^{-1} in helium atmosphere. The flow rate of the helium purge gas was 20mL min^{-1}. The interface temperature was held at 200°C. The mass spectrometer was set at an ionizing voltage of 70 eV in EI mode.

In this paper, impregnated samples will be noted as following: Cell-metal for impregnated cellulose with chloride metal. For example, Cell-Ni for $NiCl_2$ impregnated cellulose, etc.

Results and discussion

Thermal behaviour study by TG analysis

Classical characteristics of the samples thermal degradation are used in order to evaluate their behaviours, such as the initial degradation temperature (defined as the temperature corresponding to 1% of mass loss), maximum degradation rate temperature and mass loss percentage (Table 1). The mass loss (TG) and the rate of mass loss (DTG) curves are shown in Fig. 1. It can be observed that $NiCl_2$ and H_2PtCl_6 did not display obvious effects on cellulose pyrolysis (almost the same maximum mass loss rate temperature as pure cellulose) except an increase of the carbonaceous residue mass at 400°C (+10%) and some differences in initial degradation temperature values (Table 1). $ZnCl_2$ strongly changes the thermal behaviour of the impregnated sample and allows to the increase of carbon residue amount by 20%. The starting degradation temperature (T_i=215°C) corresponding to 1% of mass loss is significantly smaller than that of neat cellulose (T_i=276°C) and the maximum mass loss rate temperature is also lowered (shift of 48°C – Table 1).

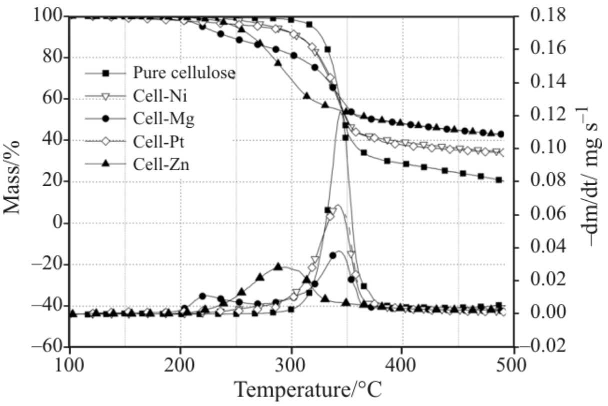

Fig. 1 TG-DTG curves for pure and impregnated cellulose

Table 1 Thermal characteristics of pure and impregnated cellulose samples

Samples	T_i^a/°C	T_m^b/°C	Mass loss/% at 400°C
Aldrich cellulose	276	343	71
Cell-Ni	231	342	61
Cell-Pt	155	341	62
Cell-Mg	165	222, 342	52
Cell-Zn	215	295	52

[a] initial degradation temperature at 1% of mass loss;
[b] maximum mass loss temperature

With $MgCl_2$, two peaks are observed; the first one in the temperature range of 165–280°C corresponds to 15% of mass loss and the second one within 280–364°C to 35% mass loss. Most likely, adding $MgCl_2$ shifts some cellulose degradation reactions to a lower temperature indicating some catalytic effect of $MgCl_2$. Moreover the $MgCl_2$ presence in cellulose promotes char formation (+20%).

To sum up, it obviously appears that the influence of the used minerals is different and leads to clear changes in the thermal behaviour of the impregnated cellulose.

Py-MS analysis of emitted vapours

Py-MS analysis from ambient temperature to 500°C was carried out with same heating rate as TG analysis. Thus, a study in a real way of the degradation reactions corresponding to the mass loss degradation of cellulose samples will be done in this part of work. The total ion current (TIC) Py-MS curves of the pure and impregnated cellulose are shown in Fig. 2. The data were normalized in relation to the sample initial mass, so that they are comparable between them. From Fig. 2 and with considering the initial degradation temperature and maximum mass loss temperature, good similarities with the TG results were noted in all cases.

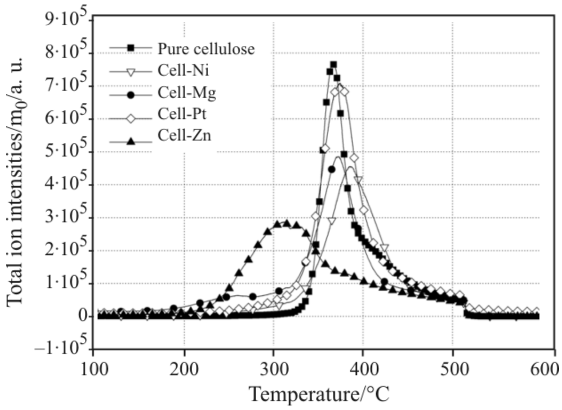

Fig. 2 Py-MS curves for pure and impregnated cellulose

To understand and clarify the effect of studied catalysts on cellulose pyrolysis, the evolved vapours and gases were analyzed. Some selected ions were chosen to represent the cellulose degradation compounds, including water (m/z=18). The production of water is of great importance in the degradation of polymers containing hydrolysable functional groups such as cellulose [37]. As discussed by Liu *et al*. [38], CO (m/z=28) and CO_2 (m/z=44) were monitored to follow the gases evolution. The remaining ions in Table 2 are representative of the vapours and they were chosen on the basis of Gomez *et al*. [39] and Liu *et al*. [37, 38] re-

Table 2 Effect of catalyst addition on chemical composition of emitted vapours

m/z	Formula	Cell-Ni	Cell-Pt	Cell-Mg	Cell-Zn
18	H_2O^+	1.0	1.0	1.3	1.4
28	CO^+	0.8	2.0	1.1	1.1
44	CO_2^+	0.8	1	1.2	1.0
30	Formaldehyde (CH_2O^+)	1.0	0.4	0.8	0.8
46	Formic acid ($HCOOH^+$)	0.8	0.5	0.8	1.9
68	Furane ($C_4H_4O^+$)	0.5	1.0	0.4	0.7
96	Furfural ($C_5H_4O_2^+$)	0.8	0.7	0.6	1.2
126	5-hydroxymethyl furfural ($C_6H_6O_3^+$)	1.6	0.9	2.5	0.9
144	Levoglucosan ($C_6H_8O_4^+$)	1.8	1.5	0.5	0.6

sults. In some cases, chlorhydric acid (*m*/*z*=36) is observed in non negligible amounts. For each ion, the peak area was calculated and normalised in relation to the pure cellulose peak area for the same ion (Table 2). Peak areas ratios accuracy is ±0.2.

Table 2 shows that the emitted vapours composition is variable from one catalyst to another which thus influences in a different way the cellulose degradation mechanism.

$MgCl_2$ effect

Figure 3b presents the evolution of some selected ions. It is clearly observed that water (and HCl) evolution starts at lower temperature (~170°C) than pure cellulose (Fig. 3a). Parallel HCl production can be attributed to the reaction of water with $MgCl_2$ [40]. Consequently, the first DTG peak for Cell-Mg (Fig. 1) can be attributed to water and hydrochloric acid formations. This demonstrates the $MgCl_2$ influence on the cellulose dehydration as it was observed by several authors [12]. The mechanisms of depolymerisation and vapour formation at higher temperature are observed in the same temperature range such as pure cellulose. The decrease of the preliminary dehydration temperature for Cell-Mg has two consequences. Firstly, to increase both char and gases yields and secondly to disfavour the depolymerisation mechanism (Table 2). These results are in agreement with those of Liu *et al*. [37, 38].

$ZnCl_2$ effect

$ZnCl_2$ is a Lewis acid that catalyses the chemical reactions of C–O and C–C heterolytic scissions [41]. As TG results (Fig. 1), $ZnCl_2$ addition on cellulose sample presents a one-step decomposition with the shifted maximum degradation temperature to lower temperature. It is demonstrated in Fig. 3c that all selected ions curves are shifted by ~60°C to lower temperatures at the exception of CO_2. It has to be noted that, in this case the CO_2 evolution between 400 and 500°C is very similar to those observed for cellulose alone and seems to correspond to solid degradation [37]. It can be assumed then, that $ZnCl_2$ is a catalyst in all pathways of cellulose degradation: dehydration, depolymerisation and ring opening leading to light oxygenated product and CO, CO_2 formation (Table 2).

$NiCl_2$ and H_2PtCl_6 effects

The maximum degradation temperature is slightly higher (~10–20°C) than that of pure cellulose (Fig. 3d and e). Apparently, $NiCl_2$ and H_2PtCl_6 addition does not contribute much to catalyse the cellulose degradation reactions. Nevertheless, both catalysts favour the anhydrosugars formation at the expense of formic

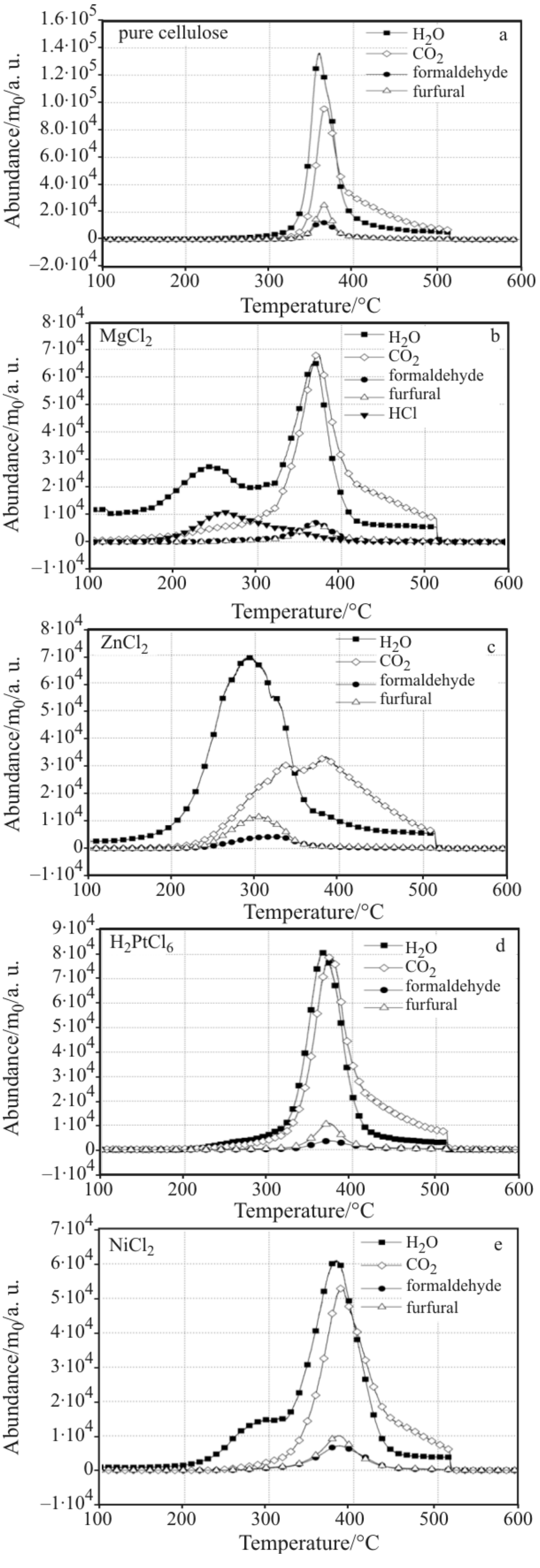

Fig. 3 Py-MS curves of selected ions for pure and impregnated cellulose, a – pure cellulose, b – Cell-Mg, c – Cell-Zn, d – Cell-Pt and e – Cell-Ni

acid, formaldehyde and in general furanic derivatives (Table 2). Probably, the increase of degradation temperature can explain the increasing of depolymerisation products (anhydrosugars).

Conclusions

It clearly appears that the studies minerals, in our conditions, play different roles in the thermal degradation of cellulose. Moreover, the used analytical techniques allow the rapid identification of the changes in the cellulose decomposition mechanism. Schematically, the Mg^{2+} effect is to catalyse primary dehydration reaction leading to the increase of solid residue but do not influence strongly the depolymerisation and the vapours production. $ZnCl_2$ has the most prominent effect by a catalytic role in all degradation mechanism occurring at lower temperature (between 60 and 70°C less than pure cellulose) leading to increases in water and gas production at the expense of vapours. $NiCl_2$ and H_2PtCl_6 influence only slightly the degradation reactions but shift the maximum mass loss to higher temperature (+10 to +20°C) and consequently, the depolymerisation mechanism is favoured.

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