

Self-catalytic pyrolysis thermodynamics of waste printed circuit boards with co-existing metals

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HIGHLIGHTS

- The co-existing metals in WPCBs has positive catalytic influence in pyrolysis.
- Cu, Fe, Ni can promote reaction progress and reduce the apparent activation energy.
- Ni play better role in promoting WPCB pyrolysis reaction.

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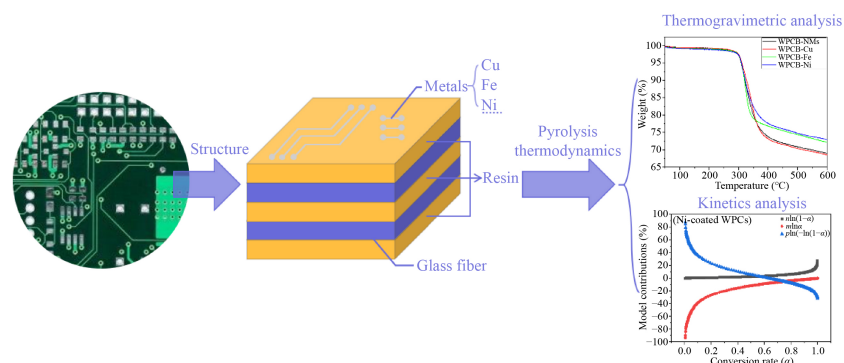
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ABSTRACT

Waste printed circuit boards (WPCBs) are generated increasingly recent years with the rapid replacement of electric and electronic products. Pyrolysis is considered to be a potential environmentally-friendly technology for recovering organic and metal resources from WPCBs. Thermogravimetric analysis and kinetic analysis of WPCBs were carried out in this study. It showed that the co-existing metals (Cu, Fe, Ni) in WPCBs have positive self-catalytic influence during the pyrolysis process. To illustrate their catalytic effects, the apparent activation energy was calculated by differential model. Contributions of different reactions during catalytic pyrolysis process was studied and the mechanism function was obtained by Sesták-Berggren model. The results showed that Cu, Fe, Ni can promote the reaction progress and reduce the apparent activation energy. Among the three metals, Ni plays better catalytic role than Cu, then Fe. This work provides theoretical base for understanding the three metals' catalytic influence during the pyrolysis of non-metal powders in WPCBs.

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1 Introduction

With the rapid replacement of electronic devices, the amount of waste printed circuit boards (WPCBs) is continually increasing. WPCBs contain multiple metals, fiberglass, resin, etc., which is considered valuable to recycle (Zhan and Xu, 2014; Evangelopoulos et al., 2015; Wang and Xu, 2015; Wang et al., 2017; Wu et al., 2017; Alenezi and Al-Fadhli, 2018). However, traditional treatment for WPCBs faces with low efficiency and second

pollution due to the complex compositions. Pyrolysis is considered as a potential technology for recovering valuable materials like organic resources from WPCBs (Quan et al., 2010; Lam et al., 2016). Quan et al. (2009) found that operating variables such as particle size and heating rate affect the reaction rate. Ma et al. (2011) investigated the thermogravimetric characteristics of WPCBs from different electronic devices. Wang et al. (2011) used Flynn-Wall-Ozawa's integration method obtaining WPCBs pyrolysis kinetics equation. Evangelopoulos et al. (2017) investigated the influence of reaction atmosphere by fixed bed reactor and found N_2 atmosphere start reaction earlier than steam. Many

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researchers also focused on catalysts effect on WPCBs pyrolysis and debromination by adding metals (Ma and Kamo, 2018; Li et al., 2019; Gao et al., 2021), metal oxides (Altarawneh et al., 2016) and other catalysts (Zhao et al., 2017; Ma and Kamo, 2019). WPCBs contain different metals such as copper, iron, aluminum, nickel, lead, silver, gold and so on (Duan et al., 2016; Chen et al., 2021; Ali et al., 2022). However, the catalytic effect on WPCBs pyrolysis of co-existing metals is not clear. Circuit boards are printed or etched with copper foil to conduct electricity, electronic components are connected to the board via iron wires and nickel are used to protect copper as etch-resistant materials. Other metals such as aluminum and precious metals are always disassembled firstly, and lead is easily evaporated during heating process. Thus, this study focused on three main metals (Cu, Fe, Ni) to investigate their self-catalytic effect on pyrolysis thermodynamics of WPCBs.

2 Experimental

2.1 Materials and methods

WPCBs were collected from Yangzhou Ningda Company, China. The WPCBs were pre-treated to remove the electronic components and were crushed to powders. Non-metal powders (NMPs) were separated from metals after multi-separation through electrostatic separator. Then, pure metal like Cu was added at a percentage of 10 wt% and mixed with the non-metal powders (named Cu-NMPs). Other experimental samples like Fe-NMPs, Ni-NMPs were prepared through the same way at equal percentage to compare their catalytic effect. After that, three metal-NMPs samples were pyrolysed and were examined by thermogravimetric analyser (TG, Mettler Toledo, Shimadzu, Japan) with argon (Ar) flow rate of 30 mL/min from 50 °C to 600 °C.

2.2 Kinetics analysis

The apparent activation energy (Ea) was determined by differential model.

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (1)$$

$$k = Ae^{-\frac{Ea}{RT}}. \quad (2)$$

Combining the kinetic Eq. (1) and Arrhenius function (2), and transferring them to the logarithmic form, the following equation is obtained:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Af(\alpha)) - \frac{Ea}{RT}, \quad (3)$$

where, A represents the pre-exponential factor, Ea was the apparent activation energy, T was temperature (K), $f(\alpha)$ means reaction mechanism function, α represents the

conversion rate as defined in Eq. (4).

$$\alpha = \frac{m_s - m_i}{m_s - m_e}, \quad (4)$$

where m_s , m_i and m_e are the initial, in-process and terminal weight of NMPs, respectively. So that Ea can be calculated by the linear fitting of $\ln\left(\frac{d\alpha}{dt}\right)_{vs} \cdot \frac{1}{T}$ without the assumption of mechanism function.

The kinetic mechanism function obtained by Šesták-Berggren model (Šesták and Berggren, 1971) can be expressed as Eq. (5).

$$f(\alpha) = (1 - \alpha)^n \alpha^m (-\ln(1 - \alpha))^p. \quad (5)$$

Its logarithmic form can be expressed as Eq. (6)

$$\ln\left(\frac{d\alpha}{dt}\right) + \frac{Ea}{RT} = \ln A + n \ln(1 - \alpha) + m \ln \alpha + p \ln(-\ln(1 - \alpha)) \quad (6)$$

The parameters n , m and p can be obtained by multiple linear regression.

3 Results and discussion

3.1 Thermogravimetric analysis

Figure 1 showed that decomposition of NMPs occurred between 290 °C and 400 °C with rapid weight loss rate and a slow weight loss occurred at a higher temperature. When the temperature reached 600 °C, the total weight loss was about 30% due to the decomposition of organic matters. A higher heating rate could lead to a higher temperature of peak weight loss rate. This trend was caused by limited efficiency of heat transfer and diffusion (Jaber and Probert, 1999). Short reaction time and more instantaneous energy during the same temperature range would slow down the time to reach thermal equilibrium (Chen et al., 2018). The decomposition occurred when volatiles' vapor pressure is higher than ambient pressure, and high temperature would hinder the diffusion.

The beginning temperature is similar with both NMPs and metal-NMPs, and they all reach a peak of weight loss when temperature comes to 310–320 °C for the cleavage of chemical bonds (Lv et al., 2016). Fe can significantly lower the reaction end temperature and accelerate the pyrolysis reaction, whereas Cu and Ni show little effects.

3.2 Kinetic analysis

3.2.1 Apparent activation energy

To further illustrate the effect of metals on the catalytic pyrolysis of NMPs, the apparent activation energy with different conversion rate was calculated. A good linear fitting result of $\ln\left(\frac{d\alpha}{dt}\right)_{vs} \cdot \frac{1}{T}$ indicates that the kinetic

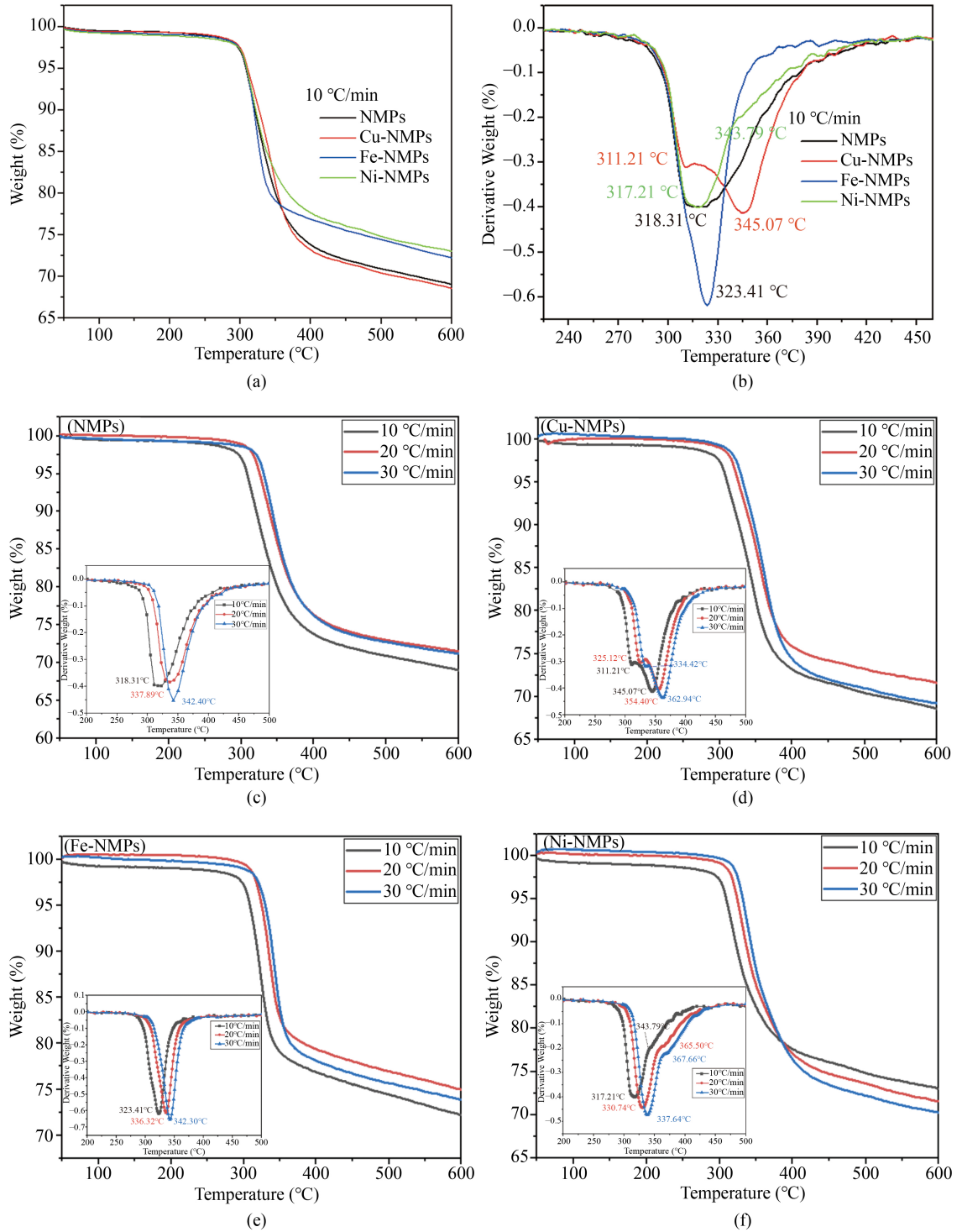


Fig. 1 Comparison of thermogravimetric and differential thermogravimetric curves of NMPs with different metals (a, b) with a heating rate of 10 °C/min, TG and DTG curves of NMPs with different metals at different heating rates (c–f).

analysis were reasonable. Based on different trend of activation energy, the reaction can be divided into three phases. For the first phase ($\alpha < 0.2$), it showed a slight decrease of activation energy. The reason is that the weak chemical bonds such as C-Br and PhO-C broke firstly at the beginning of the reaction. In the second phase ($0.2 < \alpha$

< 0.6), the activation energy gradually increased with the increasing conversion rate due to the breaking of strong chemical bonds such as C-C and C=C (Ma et al., 2015). The activation energy for the third phase ($\alpha > 0.6$) rises rapidly. The majority of the thermal decomposition reaction of resin has been completed. It is speculated that

the reaction is dominated by carbonization reforming reaction of residual char leading to high activation energy (Du et al., 2016).

From Fig. 2, a decrease in the activation energy of NMPs was observed with the addition of metal powders, indicating that three metals worked as catalysts to facilitate the NMPs pyrolysis reaction. The catalytic effect in the second phase was more significant than others and different metals have different effects on activation energy reduction.

For NMPs, the activation energies at different conversion rate range from 164.53 to 333.33 kJ/mol. The average activation energy is 245.95 kJ/mol. For Cu-NMPs, the activation energies range from 161.14 to 308.45 kJ/mol, with an average activation energy of 218.03 kJ/mol. The addition of Cu behaved a catalytic effect on breaking the C-Br bond. On one hand, for its high thermal conductivity, Cu can facilitate the heat transfer of NMPs particles from outside to inner. This promotes pyrolysis reactions and reduces the activation energy. On the other hand, the presence of Cu can obstruct mass transfer by adsorbing products and block products' diffusion channels (Natori and Natori, 2006; Gao et al., 2021). For Fe-NMPs, the activation energies range from 163.48 to 330.81 kJ/mol, with an average activation energy of 229.09 kJ/mol. The TG curves showed Fe significantly accelerated the reaction and reduced the reaction end temperature. The activation energy increased rapidly earlier than others. At the end of the reaction, Fe has little influence in the decrease of activation energy. Fe caused the surface of char residues to become denser hindering the mass and heat transfer and diffusion of the products (Chen et al., 2015). For Ni-NMPs, the activation energies range from 149.96 to 284.37 kJ/mol, with an average activation energy of 174.09 kJ/mol. Ni showed better effect on reducing activation energy of the NMPs pyrolysis reaction and promoting the reaction than other two metals. The

catalytic effect of Ni was better at high temperature (Ma and Kamo, 2018), so that the activation energy increases less in the second stage.

3.2.2 Contributions of different reactions during catalytic pyrolysis process

The Šesták-Berggren model is suitable for solving the pyrolysis of NMPs, which is independent of the assumed model formulation and avoids the errors caused by the assumed mechanism function. The relevant fitting parameters of the Šesták-Berggren model are expressed in the following mechanism functions. The regression coefficients (R^2) of mechanism functions are greater than 0.95, indicating that these fitting results are credible.

For NMPs:

$$\frac{d\alpha}{dt} = 5.92 \times 10^{47} \times [(1-\alpha)^{-1.21} \alpha^{11.5} (-\ln(1-\alpha))^{-9.7}] e^{-\frac{246 \text{ kJ/mol}}{RT}} \quad (7)$$

For Cu-NMPs:

$$\frac{d\alpha}{dt} = 2.97 \times 10^{42} \times [(1-\alpha)^{-2.3} \alpha^{13.7} (-\ln(1-\alpha))^{-12.1}] e^{-\frac{218 \text{ kJ/mol}}{RT}} \quad (8)$$

For Fe-NMPs:

$$\frac{d\alpha}{dt} = 1.09 \times 10^{44} \times [(1-\alpha)^{-16.6} \alpha^{-29.5} (-\ln(1-\alpha))^{31}] e^{-\frac{227 \text{ kJ/mol}}{RT}} \quad (9)$$

For Ni-NMPs:

$$\frac{d\alpha}{dt} = 1.69 \times 10^{28} \times [(1-\alpha)^{-2.3} \alpha^{10.5} (-\ln(1-\alpha))^{-9.9}] e^{-\frac{149 \text{ kJ/mol}}{RT}} \quad (10)$$

These mechanism functions indicate that different metals have different effects during the process of the pyrolysis reaction.

The contributions of the Šesták-Berggren model at the different pyrolysis phases are analyzed in Fig. 3. In this function, $(1-\alpha)^n$, α^m and $(-\ln(1-\alpha))^p$ respectively represent the mechanisms of phase boundary reactions, diffusion reactions and nucleation reactions.

For Cu-NMPs and Ni-NMPs, the value of $p \ln(-\ln(1-\alpha))$ was large and positive in the first phase of the pyrolysis process. This indicated that Cu and Ni promoted nucleation reactions at the reaction initiation phase because the sufficient reactants made the pyrolysis of NMPs more likely to occur. The diffusion reaction represented by $m \ln \alpha$ was the step controlling the rate. In the second phase, the values of $p \ln(-\ln(1-\alpha))$ and $m \ln \alpha$ gradually decreased while $n \ln(1-\alpha)$ gradually increases. The contribution of the nucleation and diffusion reactions decreased as the reactants are consumed. In the third phase, only the phase boundary reaction promoted the pyrolysis reaction slightly. The reactants was almost depleted so that the nucleation and diffusion reactions had

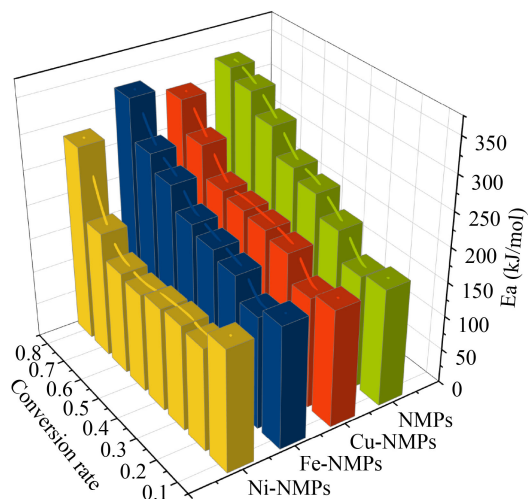


Fig. 2 Comparisons among NMPs and metal-NMPs.

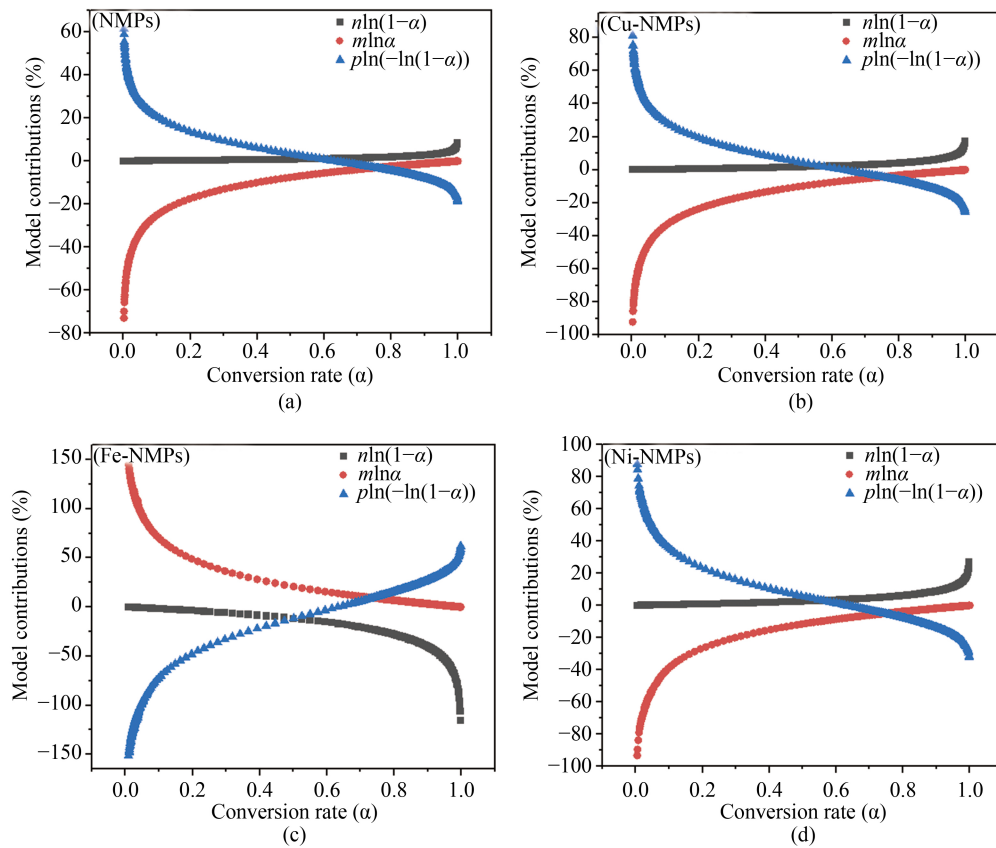


Fig. 3 Model contributions of NMPs (a), Cu-NMPs (b), Fe-NMPs (c) and Ni-NMPs (d).

no positive effect on the pyrolysis reaction anymore.

For Fe-NMPs, the diffusion reaction promoted the reaction in the first phase, letting products leave reaction system quickly and accelerating the reaction. However, as reactants were consumed and the production rate decreased, the promotion effect by the diffusion reaction gradually diminished. The value of nucleation reaction's contribution gradually increased and promoted the pyrolysis. Due to the dense surface of char residues (Chen et al., 2015), the phase boundary reaction inhibited the whole pyrolysis process and intensified at the end.

4 Conclusions

This work illustrated that the co-existing metal was beneficial to NMPs' pyrolysis process, which plays the self-catalytic role. The apparent activation energy and mechanism function of non-metal powders in WPCBs and metal-NMPs were calculated. It was proved that metal catalysts all reduced the activation energy of pyrolysis reaction. Moreover, Ni play better role in promoting NMPs pyrolysis reaction, in the order like Ni>Cu>Fe. The further study could focus on catalytic mechanisms of co-existing metals at the atomic or molecular level and combining the effect on debromination.

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