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TG–FTIR analysis of pyrolusite reduction by major biomass components[☆]Yunfei Long¹, Le Ruan², Xiaoyan Lv¹, Yiju Lv², Jing Su¹, Yanxuan Wen^{1,*}¹ School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China² College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China

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ABSTRACT

Pyrolusite reduction processes by three major biomass components cellulose, hemicelluloses and lignin, represented by CP, HP and LP, respectively, were investigated by thermogravimetric analyzer coupled with Fourier transform infrared spectrometry (TG–FTIR). The Šesták–Berggren (SB) equation was used to evaluate the kinetics of reduction processes. TG analysis reveals that the main reduction processes occur at 250–410 °C, 220–390 °C, and 190–410 °C for CP, HP, and LP, respectively. FT-IR and XRD results indicate that various reducing volatiles (e.g. aldehydes, furans, ketones and alcohols) are produced from the pyrolysis with the three major components, which directly reduce MnO₂ in ore to MnO. The processes are described by the SB equation with three parameters (*m*, *n*, *p*). Their non-zero values suggest that pyrolusite reduction is controlled by the diffusion of reducing gaseous products through an ash/inert layer associated with minerals. The apparent activation energies for pyrolusite reduction by CP, HP and LP are 40.48, 25.70 and 40.10 kJ·mol⁻¹, respectively.

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1. Introduction

Manganese is widely used in many fields, such as steel production and preparation of dietary additives, fertilizers, cells and fine chemicals. Because of gradual depletion of high-grade manganese ores, many efforts have been made to meet the ever increasing demand for manganese by recovering it from low-grade pyrolusite. The stability of manganese oxide (MnO₂) in pyrolusite under acid and alkaline oxidizing conditions enables manganese extraction from pyrolusite under reducing conditions. Generally, there are two major technical routes to reduce pyrolusite by hydrometallurgical and pyrometallurgical reductions [1]. Hydrometallurgical reduction uses reducing agents (SO₂, molasses, glucose, H₂O₂, FeSO₄, etc.) to reduce manganese dioxide from the ores under acid medium [1,2], but this method is not widely applied in commercial practices because of its complex purification process and serious water-pollution hazards [2]. Pyrometallurgical reduction with coal as reducing agent is a conventional technology for treating low-grade pyrolusite [1,3], but it produces numerous pollutants, including smoke dust, oxysulfides, and nitrogen oxides [1,4]. Moreover, it requires a reaction temperature over 900 °C, which is too high for most reactors [1,5–7]. Thus it is highly important to develop a clean, energy-saving and environment-friendly route to reduce the low-grade pyrolusite.

Recently, the potential of biomass wastes, such as sawdust, straw, cornstalk, bagasse and bagasse pith, as reducing agent have been investigated to overcome above problems [8–14]. Results show that biomass

can reduce MnO₂ in ores at temperatures below 600 °C with reduction higher than 95%. Cheng *et al.* [11] have reported that low-grade MnO₂ ores can be totally reduced by cornstalk biomass at 500 °C. Yang *et al.* [12] and Long *et al.* [13] have found that low-grade pyrolusite can be completely reduced by bagasse at 450 °C. Zhou *et al.* [14] have also reported that pyrolusite can be reduced by bagasse pith at 350 °C. Biomass reduction is a zero emission process, because the amount of CO₂ produced during reduction is equal to that absorbed during biomass growth [15]. Hence, biomass is an environment-friendly, energy-saving, and low-cost reducing agent for reducing MnO₂ from ores.

A comprehensive understanding on the thermal reduction process and kinetics is necessary for efficient biomass reduction of pyrolusite. Fourier transformation infrared spectrometry (FT-IR) and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) results indicate that thermal reduction of pyrolusite is related to biomass pyrolysis [13,16]. Based on the first-order reaction hypothesis, Coats–Redfern method [17] has been used to determine the activation energy of non-isothermal reduction of MnO₂ ore by biomass, such as straw, sawdust, wheat stalk and bamboo, and some valuable conclusions and insights have been obtained [18–20]. However, investigation of kinetics for each biomass is impossible because of their wide variety. Therefore, a general kinetic equation is necessary to describe the reduction of pyrolusite by different biomass.

All types of biomass contain three major components, cellulose, hemicelluloses and lignin [21]. Each component has different molecular structure and nature and different pyrolysis characteristics, and generates different gas products, resulting in different pyrolusite reduction behavior [22–25]. Biomass reduction of low-grade pyrolusite ore can be considered as the superposition of the reduction behavior of the three major components. Therefore, elucidation of the reduction

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behavior of each component and their interactions is essential to better understand the reduction mechanism and obtain a general kinetic equation on reduction of pyrolusite. However, results on each biomass component and their interactions in the pyrolusite reduction are limited.

In this study, processes of pyrolusite thermal reduction by the three major components of biomass are investigated. The pyrolysis of each component and their effects on the pyrolusite reduction are analyzed by TG/DTG–FTIR experiments. The Šesták–Berggren (SB) equation with three parameters is used to describe the kinetic behavior of pyrolusite reduction. The information obtained in this study is useful to better understand the biomass reduction of pyrolusite and provides valuable insights in the development of general kinetic equation.

2. Materials and Methods

2.1. Materials

Pyrolusite was collected from Guangxi, China, containing Mn 22.01 wt%, Fe 11.16 wt%, SiO₂ 27.62 wt%, Al₂O₃ 10.93 wt%, CaO 0.09 wt%, MgO 0.12 wt%, S 0.020 wt%, and P 0.181 wt%. The ore samples were crushed to 0.147 mm (100 mesh). Cellulose was purchased from Beijing Chemical Reagent Company (Beijing, China). Xylan (extracted from beech wood and often used as a representative compound for hemicelluloses) and lignin were obtained from Sigma-Aldrich Corp. (MO, USA). The cellulose, hemicellulose and lignin were mixed and tested without further treatments. Pyrolusite was mixed with cellulose, hemicellulose or lignin at a mass ratio of 10:1, based on the previous results [13]. Pyrolusite reduction processes by cellulose, hemicellulose and lignin are labeled as CP, HP, and LP, respectively.

2.2. TG–FTIR

A thermogravimetric analyzer (Q50TGA, TA, DE, USA) was coupled with a FT-IR spectrophotometer (Nicolet6700, OMNIC) to investigate the mass loss and on-line evolution of gaseous products from the pyrolysis. In the TGA experiment, the sample was heated from room temperature to 800 °C at 20 °C·min⁻¹ under N₂ at a flow rate of 40 ml·min⁻¹ to maintain an inert atmosphere for decomposition. The FT-IR was connected to TG by a flow cell, which was heated to 180 °C to prevent condensation of produced gas on the cell wall. The scanning range was set to be 600–4000 cm⁻¹. Considering the time required for N₂ to flow and fill the spectrometer cell volume, the start time difference between FT-IR and TG is about 4 min. To reduce the influence of sample amount on IR absorption intensity, the mass of each sample was (15 ± 0.05) mg.

2.3. XRD analysis

Ore samples before and after heating were characterized by powder X-ray diffraction (XRD, Rigaku model D/max-2500) to determine the mineralogical composition. The diffractogram obtained was identical to standard diffraction mineral patterns.

2.4. Kinetic model background

The kinetics of heterogeneous reaction processes is described as different equations by taking into account special features of their mechanisms. The reaction rate ($d\alpha/dt$) can be expressed by conversion α .

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}, \frac{d\alpha}{dt} = \frac{d(\Delta m)}{(m_0 - m_f)dt}, \frac{d\alpha}{dT} = \frac{d(\Delta m)}{(m_0 - m_f)dT} \quad (1)$$

where $\frac{d(\Delta m)}{dt}$ and $\frac{d(\Delta m)}{dT}$ can be directly obtained from DTG data.

When temperature increases at a constant rate ($\frac{dT}{dt} = \beta = \text{const}$), the non-thermal kinetic equation of a process can be written as [26,27]

$$\frac{\beta d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha). \quad (2)$$

The kinetic function $f(\alpha)$ for a heterogeneous reaction depends on the reaction mechanism. The SB equation represents a generalized function to describe heterogeneous reaction kinetics and it is a powerful tool to deal with kinetic data by model-fitting methods [28–30]:

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \quad (3)$$

where m , n , and p are generally non-integer exponents. The SB equation with three parameters is commonly abbreviated as SB(m, n, p) equation. Different values of m , n and p describe various probable mechanisms, as classified in Table 1. Therefore, the equation can describe the kinetics of complex heterogeneous reaction processes.

Table 1
Mechanism of rate-limiting stages using m , n and p values

m	n	p	Rate-controlled stage
0	0	-1	2D diffusion (Valensi equation).
1	1	0	Branching nuclei (Prout–Tompkins equation).
0	0	0	1D interface boundary movement or flat surface evaporation.
≠0	0	0	Formation of nuclei on power or exponential law, latter stage of nuclei linear growing, 1D diffusion (parabolic law).
0	≠0	0	2D and 3D interface boundary movement (cylindrical or spherical symmetry) or n th kinetic order.
0	≠0	≠0	2D and 3D nuclei growth (Avrami–Erofeev equation), accelerating or decelerating rate of nuclei growth.
≠0	≠0	≠0	Diffusion through an ash/inert layer (Jander equation, G-B equation, Z-L-T equation, anti-Jander equation, anti-G-B equation, anti-Z-L-T equation, etc.), or any complicated case unjustified yet.

Substitution of Eq. (3) into Eq. (2) gives the following general differential equation

$$\frac{\beta d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p. \quad (4)$$

Taking the logarithm of Eq. (4), the following equation is obtained.

$$\ln\left(\frac{\beta d\alpha}{dT}\right) = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} + m \ln \alpha + n \ln(1-\alpha) + p \ln[-\ln(1-\alpha)] \quad (5)$$

3. Results and Discussion

3.1. Thermal analysis

TG/DTG experiments were conducted to measure the mass change during the pyrolysis of the three biomass components and the reduction of pyrolusite under N₂ at a 20 °C·min⁻¹ heating rate. Fig. 1 shows these TG/DTG curves. Each pyrolysis process can be divided into three stages [31,32]. In the first stage (below 200 °C), mass is lost in sample drying and most of the moisture is released. The second stage involves fast thermal decomposition processes and contributes to the major mass loss. The last stage is high-temperature charring of the residue with minimal mass loss. In the second stage, decomposition processes of cellulose, hemicelluloses and lignin occur at 290–400, 180–370, and 200–580 °C, respectively. Compared with the narrow peaks of cellulose and hemicellulose, lignin has a wide mass-loss peak. Cellulose and lignin have a single peak, while hemicellulose presents two peaks. The maximum values of DTG curves (mass-loss rate) of

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