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Effects of nano nickel powders addition on flash pyrolysis of poly(ethylene glycol)

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Abstract

Pure PEG and the mixture of PEG and nano nickel powders (PEG/n-Ni) were pyrolyzed at 500 °C for 5 min in N_2 atmosphere. GC/MS and FTIR were employed to detect the volatile products. Some important regularity in the mass spectra of the PEG pyrolysis products was discovered, and 11 series of PEG pyrolysis products were identified. The experimental results show that the nano Ni powders evidently change the relative contents of each products series. The statistical results of the ratio of C–O cleavage to C–C cleavage, as well as the ratio of hydrogenation to dehydrogenation, indicate that nano Ni powders have remarkable effects on the bonds cleavage and free radicals annihilation. The process of hydrogenolysis and hydrogenation were propounded to explain the effects of nano Ni addition on PEG flash pyrolysis.

Keywords: Poly(ethylene glycol); Nano nickel powders; Flash pyrolysis products; End groups; Catalysis capabilities

1. Introduction

The approach and mechanism of poly(ethylene glycol) (PEG) pyrolysis have been widely studied, and the pyrolysis products were detected by various experimental methods [1–5]. Madorsky et al. identified low-weight PEG pyrolysis products around 350 °C and proposed two major chain scission types of PEG thermal degradation pathways [1]. Voorhees et al. studied the PEG pyrolysis products at 450 °C and 550 °C, and identified five major series of products by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR). The pyrolysis products observed in their experiments could be explained well via a free radical decomposition scheme [2]. Arisawa et al. studied flash pyrolysis of PEG at 370–550 °C by T-jump/FTIR spectroscopy. They concluded that the major volatile pyrolysis products contained hydroxyl, 'methyl ether' and 'ethyl ether' end groups [3]. Lattimer carried out the PEG pyrolysis in low temperature range 150–325 °C and characterized eight series of oligomeric pyrolysis products by matrix-assisted laser desorption/ionization mass spectrometry (MALDI/MS) and direct chemical ionization (isobutane CI/MS). Their experiments indicated that the decomposition scheme was free radical in nature and the relation between the bonds cleavage and the experimental temperatures was very close [4]. Pielichowski et al.

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studied PEG pyrolysis by thermal gravimetric analysis (TG), TG/FTIR and TG/MS, and identified a number of low-molecular weight products [5].

PEG has also been investigated as a binder of solid propellants, and the volatile PEG pyrolysis products are of special interesting [3,6]. The volatile PEG pyrolysis products, especially under the condition of flash pyrolysis, are possibly the reactants in the flame zone of PEG. The effects of nano nickel powders on the thermal and combustion properties of the oxidizers of propellants have been widely studied and reported [7–13]. Most of the researches showed that nano nickel powders had good catalytic effects on the thermal decomposition or combustion of oxidizers. For example, the high decomposition temperature of oxidizer ammonium perchlorate decreased by 112.9 °C and the total heat release increased remarkably from 0.436 to 1.32 kJ g^{-1} by adding 5% nano nickel powders [10]. However, few works has reported about the effects of nano-metal powders on the pyrolysis of propellant binder PEG.

In the present work, GC/MS and FTIR were employed to detect the volatile products from flash pyrolysis of pure PEG (p-PEG) and the mixture of PEG and nano nickel powders (PEG/n-Ni). The effects of nano Ni powders addition on the PEG flash pyrolysis therefore can be known by analyzing the products both from p-PEG and PEG/n-Ni pyrolysis.

2. Experimental

2.1. Samples

Poly(ethylene glycol) 2000 was supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Nano Ni powders are supplied by Shengtai Nano Co., Ltd, Jilin, China, and the average grain size is 68 nm.

PEG/n-Ni sample was prepared as following: the pure PEG (solid state at room temperature) was heated to melt carefully, nano Ni powders were added into the regularly stirred melted PEG, the mixture was cooled quickly and stored in a sealed container after the needed amount of nano metal powders were added and uniformly dispersed. The mass ratio of PEG and nano Ni powders for the prepared PEG/n-Ni sample is 10:1.

2.2. Pyrolysis

The pyrolysis system is made up of a tubular heater, a temperature controller, a quartz tube, a quartz boat and a U-tube collector. Most of the devices and their operation have been detailedly described in Ref. [14], but a U-tube collector was used in our experiments instead of the Cambridge pad assembly reported in Ref. [14]. A schematic of the pyrolysis system is showed in Fig. 1. The U-tube collector was placed in a water/ice/salt bath, and about 5 ml CH_2Cl_2 was injected into the collector before experiment each time. 0.2 g sample was pyrolyzed for 5 min in N_2 atmosphere for each experiment. After pyrolysis, about 25 ml CH_2Cl_2 was injected into the U-tube collector to dilute the products. The solution in the collector after experiment was then transferred into a Kuderna-Danish concentrator and was concentrated to about 1 ml, preparing for products analysis.

2.3. Pyrolysis products analysis

The collected products were analyzed by Thermo Finnigan GC/MS using Varian cp-sil 8cb capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness), with the following temperature programming: the initial oven temperature was 40 °C, holding for 2 min, and then was heated to 250 °C with the heat-

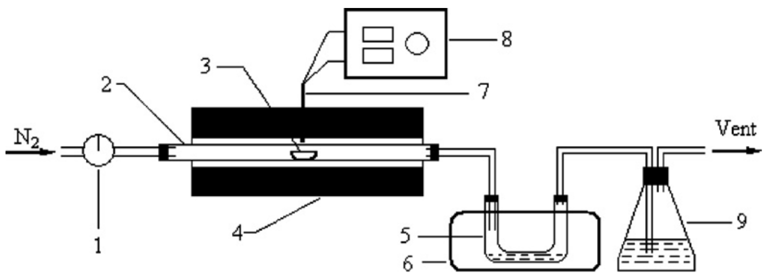

Fig. 1. A schematic of the pyrolysis system: (1) flow meter, (2) quartz tube, (3) quartz boat, (4) tubular heater, (5) U-tube collector, (6) water/ice/salt bath, (7) thermocouple, (8) temperature controller, (9) NaOH solution.