PRODUCTION OF HYDROGEN AND CARBON MATERIALS FROM POLYPROPYLENE BY COMBINED CATALYSTS

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Abstract

Feedstock recycling is of great interest environmentally for providing a suitable method treating waste plastics. Synthetic polymers, especially polyolefin, consist of carbon element and hydrogen element, in which the content of hydrogen element is 14.3 wt %. Thus the used polyolefin is an affluent resource for the production of carbon materials and hydrogen energy. In previous studies, we have found that the combination of solid acid and nickel catalyst could efficiently promote the conversion of virgin or waste polypropylene into carbon nanotubes and hydrogen. In this report, we systematically explored the effects of halogenated compounds combined with nickel catalyst on the yield and morphology of the produced carbon nanotubes. The results showed a synergistic catalysis of these materials with nickel catalyst in promoting the formation of carbon materials and the production of hydrogen. The work offers a new potential way to transform waste plastics containing halogenated additives into carbon materials and hydrogen.

Keywords: *Polypropylene, combined catalysts, carbon nanotube, nickel catalysts, hydrogen.*

1. Introduction

Polyolefin, which consist of carbon element and hydrogen element, is widely applied in the modern society. Thus the used polyolefin is an affluent resource for the production of carbon materials and hydrogen energy. It is a hard and necessary task to find a suitable method treating waste plastics for feedstock recycling. In previous studies, we have found that the combination of solid acid and nickel catalyst could efficiently promote the conversion of virgin or waste polypropylene (PP) into carbon nanotubes and hydrogen [1-3]. However, the composition of a real polymer material is very complex. For instance, a lots of polymer materials contain halogen-contained flame retardants for safe consideration. In this report, we focus on the effects of halogenated compounds (combined with nickel catalyst) on the yield and morphology of the carbon materials via the carbonization of PP.

2. Materials and Methods

Polypropylene (PP) with melt flow index of 0.8 g/min was mixed with Ni_2O_3 (from Lingfeng Chemical Company of Shanghai) and inorganic solids in a Brabender mixer at 100 rpm and 190 ^oC for 10 min. The concentration of Ni_2O_3 was 5 wt % [4-5]. The above PP mixture was put into a crucible or a fixed bed reactor and pyrolyzed at designated temperature.

3. Results and Discussion

As we know, chlorinated paraffin is one of flame retardants used in the recipe of polymer materials. Thus some used polymers, such as PP, contained this kind of halogenated compounds. Fig. 1 shows the dependence of the yield and microstructure of char on the content of chlorinated paraffin. When the content of chlorinated paraffin is lower than 0.5 wt%, the char yield increased sharply, and the morphology of the produced carbon varied with increasing chlorine content.

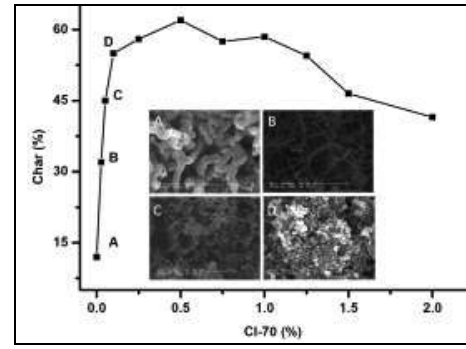

Fig. 1. Dependence of the yield and microstructure of char on the content of chlorinated paraffin (Cl-70) in crucible at 820 °C.

We further found that many halogenated compounds showed a synergistic effect with nickel catalysts on the carbonization of PP, such as decabromodiphenyl ether, NH_4Br, $FeCl_3$, CuCl and so on. In the cases of PP and PP mixtures with halogenated compounds, the yields of residual char were zero, meaning that halogenated compounds or their derivatives could not catalyze the

carbonization of the degradation products under the experimental conditions. When a small amount of halogenated compounds was added into mixture of PP/Ni_2O_3, the char yield was greatly promoted comparing with that from PP/Ni_2O_3 composite, indicating the synergistic effect between halogenated compounds and Ni_2O_3 on the formation of residual char. A similar phenomenon was also observed in the combination between chlorinated carbon nanotubes and nickel catalyst.

Fig 2 presents the effect of Cl/Ni molar ratio on the char yield of PP during combustion experiments at 820 °C. After adding just 0.060 wt% CuCl (Cl/Ni=0.0100) to PP/5.0Ni_2O_3, the char yield increases rapidly from 4.5 to 29.9 wt%. Then the char yield goes up rapidly with increasing CuCl. However, after CuCl increases to 0.751 wt% (Cl/Ni= 0.125), the char yield begins to decrease. Therefore, we could conclude that, when CuCl is less than ~0.751 wt% (Cl/Ni> ~0.125), the promoting effect of Ni_2O_3 and CuCl on the char yield of PP increases with increasing CuCl; subsequently, the char yield goes up to a maximum value (Cl/Ni= 0.125), after which the promoting effect of Ni_2O_3 and CuCl on the char yield decreases with increasing CuCl. That is to say, Cl/Ni=0.125 is the optimal ratio for catalytic carbonization of PP.

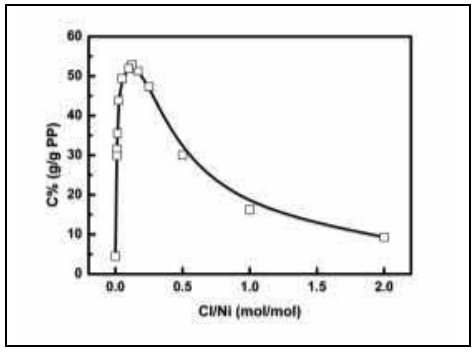

Fig. 2. Effect of Cl/Ni molar ratio on the char yield (C %) in CuCl-Ni_2O_3/PP mixture in crucible at 820°C.

A similar result was obtained in a pyrolyzer experiment. We investigated the mass balance of pyrolysis of Ni_2O_3-CuCl/PP in fixed bed reactor at different Cl/Ni molar ratio. The results showed that the char yield reached a maximum at a Cl/Ni molar ratio of 0.125. With increasing Cl/Ni molar ratio, the liquid fraction increased and the gas fraction decreased. The produced H_2 reached a maximum at a Cl/Ni molar ratio of 0.0125.

4. Conclusions

Although the presence of halogenated compounds is a trouble for preparing oil products using waste polymers, it becomes an advantage for producing carbon materials and hydrogen. The results showed a synergistic catalysis of halogenated compounds with nickel catalyst in promoting the formation of carbon materials and the production of hydrogen via the carbonization of PP. Furthermore, the content of halogenated compounds played a key role in the yield and morphology of the produced carbon nanotubes. Our latest results have showed that the above combined catalysts can also promote the carbonization of polyethylene, polystyrene and ethylene-propylene copolymers. Thus we believe that the combined catalysis is a general-purpose method for feedstock recycling of waste polymers.

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