CATALYTIC CRACKING AND DEHYDROCHLORINATION OF POLYPROPYLENE / POLYVINYL CHLORIDE USING MgO COMPOSITES

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1. Introduction

Recycling of waste plastics is of great interest due to the serious environmental problems caused by waste plastics. Among the various methods of resource recovery, polymer pyrolysis, aiming to degrade waste plastics to fuel oil or valuable chemicals for a variety of downstream processes, is the most promising technology for resource recovery from waste polymer materials. However, polyvinylchloride (PVC) in waste plastics will cause corrosion problems and a contamination of all product streams with chlorinated organics during pyrolysis. Therefore the dehydrochlorination of waste plastics is a must for this reaction. Different sorbents for dehydrochlorination were investigated, and among these sorbents, alkaline earth oxides such as MgO attracted significant attention as effective dehydrochlorination catalysts and chemsorbents. However, they are far from the requirement of realizing commercial use of this process due to the limited dehydrochlorination degree and fast deactivation of the catalysts caused by large amounts of HCl produced during the reaction. On the other hand, lowering pyrolysis temperature and increasing pyrolysis rate, which will decrease energy consumption of this process, are also very necessary for this reaction. In this paper a lanthanum modified MgO catalyst, La-MgO, and carbon-coated nano-MgO have been developed with both dehydrochlorination and catalytic cracking ability, which will be very useful in the recycling of chloride-containing waste plastics.

2. Experimental

2.1 Preparation of MgO composites

MgO/Carbon: sucrose and magnesium nitrate were dissolved in deionized water and precipitated by ammonium hydroxide until the pH value reached 9.5, then the precipitation was dried under air at 90 °C for 12 hours to obtain $Mg(OH)_2$ / Sucrose precursors. The

precursors were heated from room temperature to 500 °C at a rate of 2 °C /min and kept at this temperature for 2 hours.

La-MgO composite: magnesium nitrate and lanthanum nitrate were dissolved in deionized water and precipitated by ammonium hydroxide until the pH value reached 9.5, after the resulting suspension stayed for 1 h at this pH; the precipitate was thoroughly washed with absolute ethanol. The obtained samples were treated under air at 120 $^{\circ}$ C for 12 h and calcined at 500 $^{\circ}$ C for 5 h.

2.2 Degradation procedure and product analysis

The pyrolysis of PP/PVC was carried out in a glass reactor by batch operation. In a typical catalytic run, sorbents (2 g) were mixed with PP/PVC (10 g, in a weight ratio of PP/PVC/sorbents = 4/1/1), and reacted at 400 °C until no liquid was produced. The chlorine contents in products were analyzed by oxygen bomb combustion and the chlorine ion selective electrode method (ISE). The components of pyrolysis oils were analyzed using an GC-MS.

3. Results and discussion

The MgO/Carbon composite oxide and th La-MgO composite were adopted for pyrolysis of a typical PVC-containing plastics (polypropylene/polyvinyl chloride). For chlorine distribution (Fig.1), the carbon-coated MgO from sucrose-assisted synthesis shows prominently superior dechlorination ability than MgO: the evolved chlorine is sharply decreased to 2.1 wt % (MgO: 15.7 wt %). The increased interactions between sorbents and the produced HCl due to the higher surface area of the MgO/C composite oxides may account for the superior dechlorination ability. On the other hand, the carbon deposited on MgO nanocrystals is able to promote the decomposition of organochlorine. On the otherhand, La-MgO also shows excellent dehydrochlorination ability than MgO: the evolved chlorine is sharply decreased to 0.65 wt %. Moreover, it shows prominent catalytic cracking ability for PP/PVC.



Fig. 1 Chlorine distribution from pyrolysis of PP/PVC at 400 °C.

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