PRODUCTION OF HYDROGEN AND CARBON NANOTUBES BY CATALYTIC PYROLYSIS OF WASTE POLYPROPYLENE IN A TWO-STEP PROCESS

Jie Liu,* Zhiwei Jiang, Haiou Yu, Tao Tang

[1]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.
E-mail: liujie@ciac.jl.cn

Abstract: The efficient conversion of virgin or waste polypropylene (PP) into multi-walled carbon nanotubes (MWCNTs) and hydrogen without carbon oxides has been investigated using a two-step reaction system. The proposed process consisted of two steps: pyrolysis of PP over HZSM-5 zeolite and montmorillonite in a screw kiln reactor and the following catalytic decomposition of pyrolysis gases over the nickel catalysts in a moving-bed reactor for producing MWCNTs and hydrogen simutaneously. The effects of pyrolysis temperature, pyrolysis catalysts, decomposition catalysts and polymer modifiers on the yields and morphology of MWCNTs have been determined. MWCNTs yields increased with the pyrolysis temperature increasing from 550 to 750℃. Modification of the nickel catalyst with doping of copper promoted the yield of MWCNTs and led to a production of MWCNTs with an attractive structure. These results have demonstrated that the coupled process is an efficient system for the continuous conversion of waste PP to hydrogen and nanocarbon materials.

Hydrogen is considered as an ideal alternative clean energy source. Catalytic decomposition of hydrocarbons has been widely accepted as an attractive process for the generation of CO_x-free hydrogen and valuable carbon product. Previously reported work showed that multi-walled carbon nanotubes (MWCNTs) can be synthesized using polymer as carbon source in the presence of catalyst [1,2]. With increasing consumption of plastic products during the past decades, the accumulated plastic waste has led to serious environmental pollution. Recycling plastic waste (mostly polyolefin) to produce high value-added products has caught a great interest of scientists for economic and environmental impacts in recent years. Our findings point out that polypropylene (PP) can be reorganized to produce carbon nanotube and hydrogen over nickel catalyst [3] [4]. In this report we present a semi-continuous two-step process, in which PP or waste PP is firstly catalytically degraded over HZSM-5 zeolite in a screw kiln reactor and the produced hydrocarbons are used as a feedstock for producing MWCNTs and hydrogen simultaneously over the nickel catalyst in a moving-bed reactor.

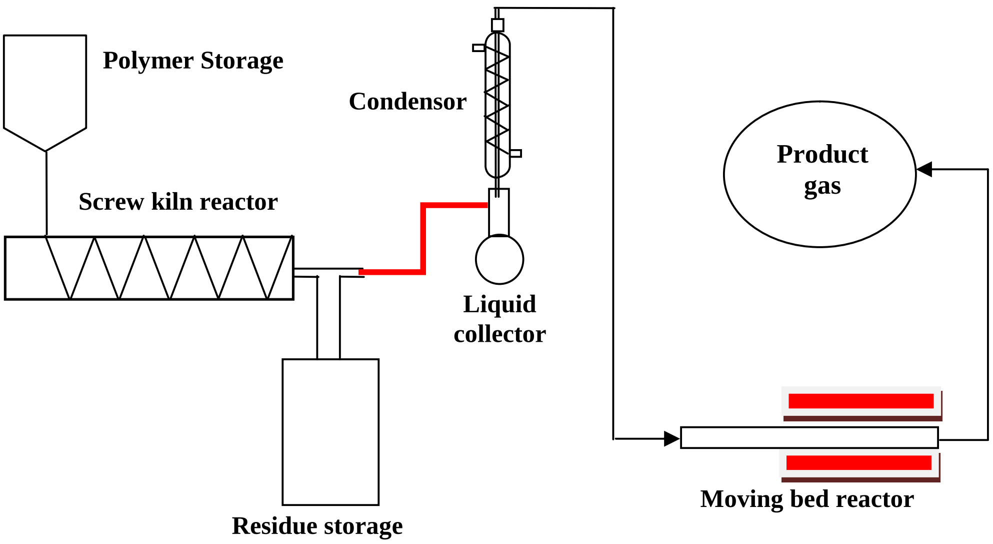

Fig. 1. Schematic diagram of the two-step reaction system.

As illustrated in Fig.1, the reaction system employed in this study is comprised of two independent reactors: a screw kiln reactor to degrade PP into a mixture of many different hydrocarbons (pyrolysis gas) and a following moving-bed reactor for producing MWCNTs and hydrogen-rich gases (product gas) simultaneously. The speed and temperature of both reactors can be adjusted as required. In a typical experiment, the moving bed reactor, the liquid collector and the residue storage were flushed with nitrogen gas for 20 min while the pyrolysis furnace and vapor deposition furnace were heated to 750 ℃ and 700 ℃, respectively. Thereafter the screw motor was switched on and the system was kept operating until steady state has been reached. Plastic feed rate remained at 80 g/h. The product gases were collected in a sample bag for 5 min and the other reaction products were collected for 30 min. 1.6 g of NiO catalyst was placed in the moving bed reactor (0.025 g/cm) whose speed is 2 rpm. The influence of pyrolysis catalysts was investigated in this work.

The pyrolysis reaction has been carried out on three kinds of ZSM-5 zeolites with Si/Al molar ratio of 25, 38 and 50. Fig. 2 shows the effect of Si/Al molar ratio of ZSM-5 zeolites on the yields of various products in the two-step reaction. The amount of product gas is about 2 times higher than that of pyrolysis gas, which can be attributed to more produced hydrogen from decomposition of the hydrocarbon mixture over nickel catalyst. According to calculation, the volume of produced hydrogen increases markedly from 13.3 to 81.4 L. The hydrogen concentration in the product gas is achieved at 73.7 vol% (Si/Al=25). With increasing Si/Al ratio, yields of the product gas decrease drastically. This can be attributed to the reduced pyrolysis gas volume and different compositions of the pyrolysis gas showed Fig. 3a, where the concentration variation of methane and hydrogen are observed with increasing Si/Al ratio. For example, the hydrogen content reduces from 21.4 to 19.5% whereas methane increases from 37.4 to 41.2%. As shown in Fig. 3b, a higher concentration of hydrogen is observed for lower aluminum content. Hydrocarbons (C2-C5) can be cracked into methane, which is also the carbon source for producing MWCNTs and hydrogen. The NiO catalyst is used without pre-reduction since the pyrolysis gas contains hydrogen, which can reduce NiO to Ni in situ. No CO and CO_2 are formed during the above process.

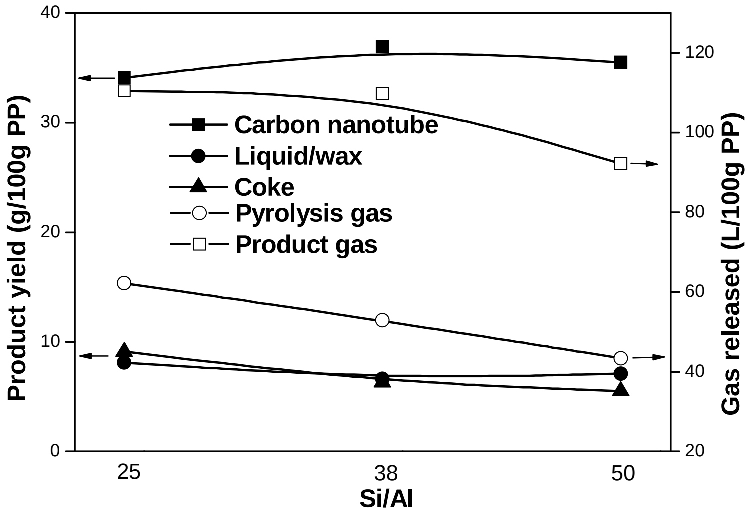

Fig. 2 Product yield from the catalytic conversion of PP in the two-step reaction system over ZSM-5 catalyst with different Si/Al molar ratio.

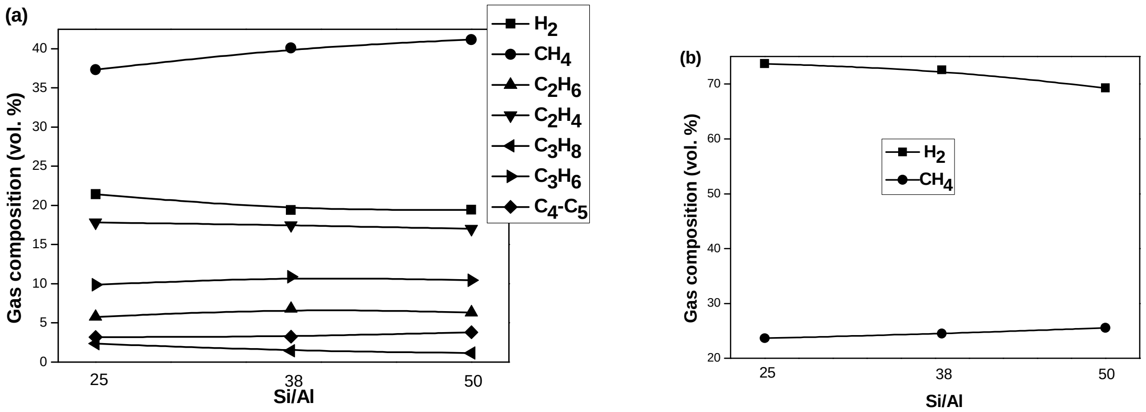

Fig. 3 Pyrolysis (a) and product gases (b) composition during two-step reaction over ZSM-5 catalyst with different Si/Al molar ratio.

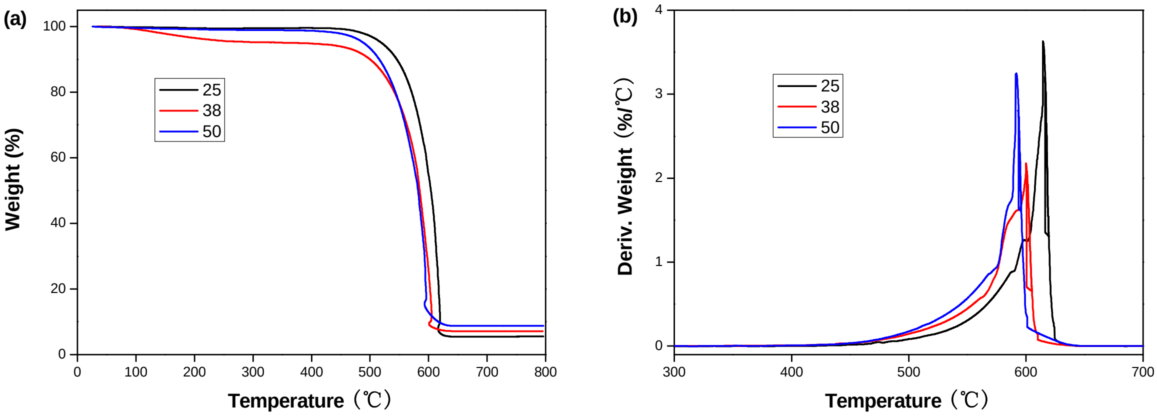

Fig. 4 TG-DTG analysis of obtained carbon products for different pyrolysis catalyst.

The TG-DTG curves of the synthesized MWCNTs using various Si/Al ratio pyrolysis catalysts are shown in Fig. 4. The higher temperature at weight loss onset and maximum weight loss reflect better graphitized MWCNTs. The formation of ideal and nonideal graphitized carbon materials in the products is observed. Using different pyrolysis catalysts with Si/Al molar ratio of 25, 38 and 50, the temperature at maximum weight loss is 615.1, 601.4 and 590.9 ℃, respectively. The residual weight decreases from 8.7 to 5.5 wt% with increasing Si/Al ratio of the pyrolysis catalysts, which indicates higher carbon yield for the low Si/Al ratio.

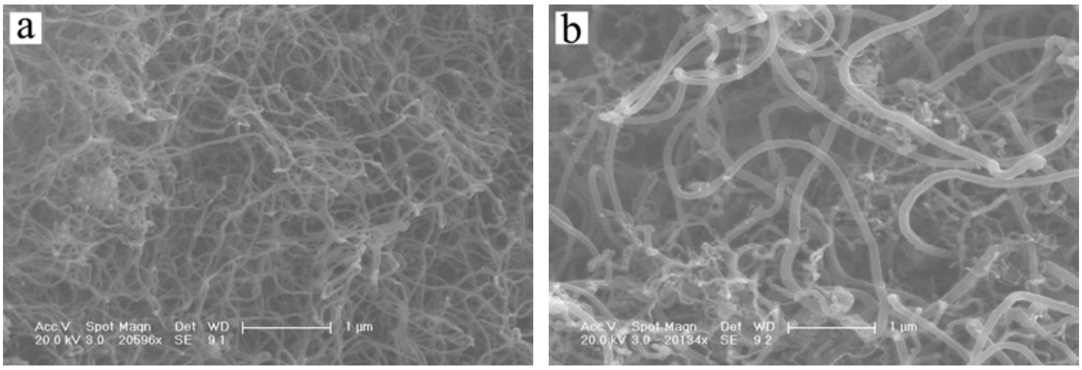

Fig. 5 SEM photographs of carbon nanotubes obtained by pyrolysis of
(a) virgin PP and (b) waste PP over ZSM-5 catalyst.

The waste PP as feedstock for producing MWCNTs and hydrogen is explored. The ash residue content of waste PP (from waste car bumper) determined by calcination in nitrogen at 700 ℃ is 11.4 wt%. SEM-EDX results suggest that the char contain silicon, magnesium, calcium, aluminum, titanium, sodium, iron, carbon and chlorine, which are related to plastic fillers probably in the form of calcium carbonate, talcum powder or coupling agent of organic titanate. The extraction experiment indicates that the waste PP contains 11.8 wt% of compatibilizers which may be EVA, POE or EPDM from IR analysis of the extracted fraction. It can be easily seen in Fig. 5 that MWCNTs with wider diameter distribution are observed when adopting the waste PP as the feedstock, and more impurity such as amorphous carbon is also found. When PP and waste PP are used as feedstock, the concentration of hydrogen in the product gas is 73.7 and 61.3 vol%, respectively, which suggests negative effect of the fillers in the waste PP on the quality of produced carbon nanotubes and the product gas composition.

In summary, pure and waste polypropylene have been pyrolyzed and decomposed in a two-step process for the simultaneous production of carbon nanotube and hydrogen. The effect of Si/Al molar ratio of ZSM-5 catalyst on the productivity of MWCNTs and hydrogen has been investigated. The pyrolysis catalyst affects the composition of the pyrolysis gas and therefore determines the quality and quantity of the products. 65.1 L/h hydrogen is produced and the volume concentration is 73.7% for 80 g/h PP feeding during the reaction. High value-added carbon nanotubes and hydrogen without CO_x are produced from low cost waste plastics. The two-step reaction system has been proved to be efficient for producing hydrogen and carbon nanotubes from waste PP, thus it is a potential technique.

Acknowledgements

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References

[1] T. Tang, X. C. Chen, X. Y. Meng, H. Chen, Y. P. Ding, *Angew. Chem. Int. Ed.* **2005**, *44*, 1517.

[2] U. Arena, M. L. Mastellone, G. Camino, E. Boccaleri, *Polymer Degrad. Stab.*, **2006**, *91*, 763.

[3] R. J. Song, Z. W. Jiang, W.G. Bi, W.X. Cheng, J. Lu, B.T. Huang, T. Tang, *Chem. Eur. J.*, **2007**, *13*, 3234.

[4] Z. W. Jiang, R. J. Song, W. G. Bi, J. Lu, T. Tang, *Carbon*, **2007**, *45*, 449.