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Microwave assisted decomposition of HDPE and PP over cobalt modified $FeAlO_x$ catalysts

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Abstract

This study examines the microwave-assisted catalytic decomposition of high-density polyethylene (HDPE) and polypropylene (PP) over cobalt-modified $FeAlO_x$ catalysts. The effects of cobalt content, reaction temperature and polymer type were investigated under temperature-controlled conditions. Increasing cobalt content favoured hydrogen-rich gas and reduced wax formation, despite a decrease in catalyst surface area. Higher temperatures further promoted hydrogen production. HDPE provided a higher hydrogen yield than PP, whereas PP formed more methane and solid residue. The results show that catalyst composition and polymer type influence product distribution during microwave-assisted polyolefin decomposition.

Keywords: HDPE; polypropylene; microwave-assisted decomposition; cobalt; mixed oxide catalysts; hydrogen.

1. Introduction

Chemical recycling provides a route for converting polyolefin waste into gases, hydrocarbons and carbonaceous materials [1, 2]. Microwave-assisted catalytic processing combines selective heating of an absorbing material with catalytic decomposition of the polymer. Iron-based materials have been investigated as microwave susceptors and catalysts for hydrogen production [3].

Catalyst composition and polymer structure affect the distribution of hydrogen, hydrocarbons and solid carbon [4-6]. This study investigates cobalt-modified $FeAlO_x$ catalysts during temperature-controlled microwave-assisted decomposition. The cobalt content was first varied using HDPE, followed by evaluation of temperature and comparison with PP.

2. Materials and methods

2.1. Materials and catalyst preparation

Commercial HDPE and isotactic PP from Sigma-Aldrich were used as model polyolefins. Catalysts were prepared by a citrate sol–gel method with nominal Co:Fe:Al molar ratios of 0:1:2, 0.1:1:2, 0.5:1:2 and 1:1:2, designated $FeAlO_x$, $0.1CoFeAlO_x$, $0.5CoFeAlO_x$ and $1CoFeAlO_x$, respectively. Metal nitrates and citric acid were dissolved in water, and the pH was adjusted to 7 with ammonia. The mixture was concentrated at 90 °C, aged at this temperature for 24 h and treated with ethanol. The catalysts were calcined in air at 400 °C for 60 min and sieved to 0.16–0.32 mm.

2.2. Microwave experiments and analysis

Experiments were performed in a PYRO microwave unit (Milestone, Italy) using 2 g polymer and 1 g catalyst under nitrogen. Samples were heated at 20 °C·min^{-1} to 300, 400 or 500 °C and held for 15 min. An infrared temperature measurement system controlled the microwave power according to the programmed temperature profile.

Gases were analysed by GC-FID/TCD using multipoint calibration and helium as an internal standard. Condensable products were extracted with dichloromethane and analysed by GC-MS. Polymers were characterized by thermal analysis and FTIR spectroscopy. Catalyst characterization included atomic absorption spectrometry, N_2 physisorption, in situ XRD, XPS and temperature-programmed desorption. Solid residues were analysed by thermo-optical carbon analysis and XRD.

3. Results and discussion

3.1. Polymer and catalyst characteristics

Thermal analysis showed that PP degraded at a lower temperature than HDPE, while FTIR spectra reflected their different molecular structures. Increasing cobalt content decreased the catalyst surface area and pore volume. The catalysts exhibited mesoporous characteristics, and ammonia desorption indicated a decrease in acidity, particularly in the stronger acid-site contribution, as cobalt content increased.

In situ XRD indicated spinel or spinel-like phases within the investigated reaction temperature range. Higher-temperature treatment produced composition-dependent phase changes. XPS spectra indicated mixed iron and cobalt oxidation states. These observations characterize the catalysts but do not independently establish the active surface state during polymer decomposition.

3.2. Hydrogen and hydrocarbon products

Gas was the main product fraction. Increasing cobalt content favoured gas formation, increased hydrogen concentration and yield, and reduced the wax fraction. The catalyst with the highest cobalt content gave the highest hydrogen production within the series despite having the lowest surface area. Catalyst surface area alone therefore did not explain the observed performance.

Raising the reaction temperature promoted hydrogen production and reduced light hydrocarbons. The largest increase in hydrogen concentration occurred between the lower and intermediate temperatures. Under the same conditions, HDPE produced more gas and a higher hydrogen yield than PP (Figure 1). PP produced more methane and solid residue.

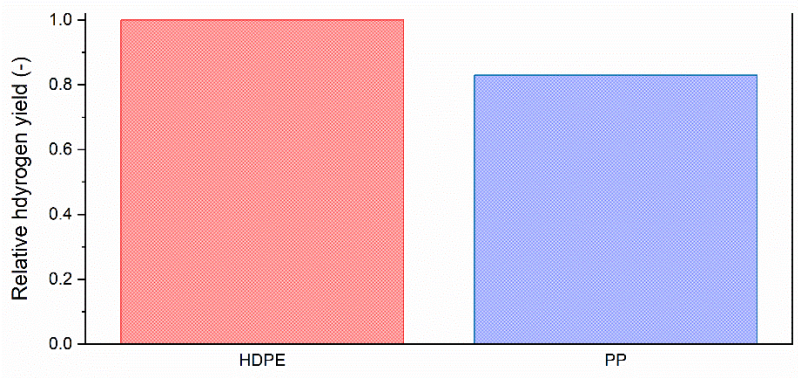


Figure 1. Relative molecular hydrogen yields from HDPE and PP over 1CoFeAlOx at 500 °C. The HDPE value is set to 1, and the PP value is expressed relative to it.

Wax composition also depended on catalyst composition, temperature and polymer type. Increasing cobalt content increased the unsaturated hydrocarbon contribution, whereas higher temperature favoured alkanes in the HDPE-derived wax. Carbon analysis of the solid residues showed a larger elemental-carbon contribution for PP than for HDPE under the same conditions.

3.3. Influence of catalyst composition and polymer type

The product trends are consistent with secondary cracking and dehydrogenation of polymer-derived hydrocarbons. Iron and cobalt sites may contribute differently to these reactions, while polymer structure affects the hydrocarbon fragments and carbonaceous residues formed [4-6]. The proposed roles of mixed oxidation states and surface acidity remain interpretations of the characterization and product data; individual reaction steps were not directly resolved.

4. Conclusion

Cobalt modification of $FeAlO_x$ influenced product distribution during microwave-assisted decomposition of HDPE and PP. Higher cobalt content and reaction temperature favoured hydrogen-rich gas and reduced wax formation. HDPE gave a higher hydrogen yield than PP, while PP produced more methane and solid residue. The results identify catalyst composition, temperature and polymer type as variables controlling hydrogen-oriented polyolefin processing.

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References

1. Geyer, R., J.R. Jambeck, and K.L. Law, *Production, use, and fate of all plastics ever made.* Science advances 2017. **3**(7): p. e1700782.
2. Lopez, G., et al., *Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review.* Renewable and Sustainable Energy Reviews, 2017. **73**: p. 346-368.
3. Jie, X., et al., *Microwave-initiated catalytic deconstruction of plastic waste into hydrogen and high-value carbons.* Nature Catalysis, 2020. **3**(11): p. 902-912.
4. Yao, D., et al., *Co-production of hydrogen and carbon nanotubes from real-world waste plastics: Influence of catalyst composition and operational parameters.* Applied Catalysis B: Environmental, 2018. **221**: p. 584-597.
5. Acomb, J.C., C. Wu, and P.T. Williams, *The use of different metal catalysts for the simultaneous production of carbon nanotubes and hydrogen from pyrolysis of plastic feedstocks.* Applied Catalysis B: Environmental, 2016. **180**: p. 497-510.
6. Williams, P.T. and E. Slaney, *Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures.* Resources, Conservation and Recycling, 2007. **51**(4): p. 754-769.