



The effect of ZSM-5 zeolite acidity on the catalytic degradation of high-density polyethylene using simultaneous DSC/TG analysis

A. Coelho^a, L. Costa^a, M.M. Marques^c, I.M. Fonseca^b, M.A.N.D.A. Lemos^a, F. Lemos^{a,*}

^a IBB – Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

^b REQUIMTE-CQF – Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Campus da Caparica, 2829 Caparica, Portugal

^c CQE – Centro de Química Estrutural, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

ARTICLE INFO

Article history:

Received 24 May 2011

Received in revised form 5 November 2011

Accepted 7 November 2011

Available online 16 November 2011

Keywords:

High-density polyethylene (HDPE)

ZSM-5 zeolite

Kinetic modelling

Acid catalysis

Catalytic degradation

Differential scanning calorimetry (DSC)

Thermogravimetry (TG)

ABSTRACT

In the present work, simultaneous thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses were used to investigate the effect of the acidity of HZSM-5 zeolites on the catalytic degradation of high-density polyethylene (HDPE). The acidity of the zeolite was modified by ion exchange with sodium. The results obtained using HZSM-5 zeolites of varying acid strengths show the effect of increasing the acidity on the reduction of the degradation temperature. The addition of sodium to HZSM-5, by ion exchange, results in a decrease of the acid strength of the catalyst and an increase in the observed degradation temperature from 402 to 465 °C.

The simultaneous use of the signals from the TG and DSC allowed the development of a kinetic model that is able to accurately describe all the runs performed, both the thermal and the catalytic degradation of the polymer. The kinetic parameters obtained clearly revealed the reduction in the activation energy due to the presence of the catalyst and its relation to the overall acidity of the samples. The gases evolved from the pyrolysis of polyethylene were also analysed using gas chromatography, and it was also found that volatile product selectivity changes with the catalyst acidity.

The fact that the overall activity for the catalytic cracking of HDPE on these zeolites varies with internal acid strength of the zeolite indicates that the inner surface of these zeolites participates in this reaction despite the fact that the reactant molecules are extremely large.

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1. Introduction

In view of their versatility and relatively low cost, the consumption of plastics and, consequently, the amount of plastic waste are growing year after year. According to the Association of Plastics Manufacturers in Europe (APME) [1], in 2009 the total world production of plastics reached over 230 million tonnes, of which 24% were produced in Europe (EU27, Norway and Switzerland). Of the 45 million tonnes of plastics used in these countries in 2009, 24.3 million tonnes were recovered but only 13.1 million tonnes were reused (54%), either through recycling or energy recovery. The remaining 11.2 million tonnes were sent to disposal facilities (46%).

The disposal of used plastics constitutes an important environmental problem mainly due to their chemical inertness and low biodegradability and, nowadays, this is one of the major concerns for the scientific community as well as environmentalists [2]. It is necessary to develop new sustainable solutions other than

incineration and disposal at landfills. The thermal and catalytic degradation of polymers is one promising alternative that allows their conversion into gaseous and liquid hydrocarbons [3,4] which can be incorporated into the liquid fuels pool.

However, the thermal degradation of plastic waste requires high temperatures, which usually results in poor quality products, making this process economically unfeasible. This method can be improved by the addition of catalysts, namely zeolites; zeolites, due to their characteristic strong acidity and ability to crack large hydrocarbons, reduce the processing temperature and time and permits the production of valuable hydrocarbon products [4–7].

Several catalysts have been used for the cracking of polymeric materials: zeolites (HZSM-5, USY, H-Beta, etc.) and mesoporous materials such as MCM-41 are some of the most important because of their particular porous structures and acid properties [4–18]. The use of different processes, such as dealumination [19], ion exchange [7], desilication and microwave irradiation in sequence [20], has been employed in this type of reaction, in order to modify the properties of the zeolites such as their thermal stability, catalytic activity and acidity.

The catalytic degradation of polymers can be evaluated using different techniques and reactors [11–15]. Due to the nature of the

* Corresponding author. Tel.: +351 21 841 7890; fax: +351 21 841 7246.

E-mail address: francisco.lemos@ist.utl.pt (F. Lemos).