STUDIA UBB CHEMIA, LVI, 4, 2011 (p. 27 - 40)

GS-MS AND FTIR STUDIES OF THE LIQUID PRODUCTS OBTAINED BY THERMAL AND CATALYTIC DEGRADATION OF POLYSTYRENE WASTE*

MIUŢA RAFILA FILIP[a,b,*], AURELIA POP[b], TIBERIU RUSU[a]

ABSTRACT. In this paper, gas chromatography mass spectrometry (GC-MS) and Fourier-transform infrared spectrometry (FTIR) were used to study the liquid products obtained from the thermal and catalytic degradation of polystyrene waste (PS) in order to establish the conditions for the best conversion degree of polystyrene waste into styrene monomer. The polystyrene waste was submitted to a thermal degradation process at 380°C and 430°C respectively, in absence and in presence of different types of metallic oxides as catalysts in a ratio of 1/10 in mass, catalyst/PS. The used catalysts were: amphoteric solids, two types of alumina; acidic solid, silica gel and basic solids, calcium oxide and copper oxide 13% deposited on alumina. Gas and liquid products and a residue were obtained by the degradation process of polystyrene waste. The yields for all obtained liquid products at both temperatures were between 83 and 89%. The GC-MS results showed that the liquid products contain mainly toluene, ethylbenzene, styrene monomer, (1-methylethyl) benzene and α-methylstyrene. The FTIR spectra of liquid products indicated the specific vibration bands of the functional groups of their compounds. The obtained results showed that the most efficient catalyst used in the thermal degradation of polystyrene waste was silica gel, for which it was obtained the largest amounts of styrene monomer at both temperatures (68.76% at 380°C and 73.16% at 430°C).

Keywords: *polystyrene waste, thermal and catalytic degradation, GC-MS, FTIR, styrene monomer*

INTRODUCTION

Polystyrene and its related products are not biodegradable in the natural environment and cause serious environmental problems. The polystyrene waste represents 10% of the plastic packaging in the residential waste stream. Therefore their recycling is important for both economical and ecological reasons.

---

* This paper was presented at the “17th International Symposium on Separation Sciences. News and Beauty in Separation Sciences, Cluj-Napoca, Romania, September 5-9, 2011”

[a] Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, 103-105 Muncii Avenue, 400641, Cluj-Napoca, Romania

[b] Babeş-Bolyai University, Raluca Ripan Institute for Research in Chemistry, 30 Fântânele Street, 400294 Cluj-Napoca, Romania, * *filip_miuta@yahoo.com*

Polystyrene is one of the most used materials in the modern plastic industry due to its excellent physical properties and low cost. The recycling of polystyrene can be done using mechanical, chemical and thermal methods. The liquid and gaseous products resulted from the degradation process of polystyrene is highly dependent on the reaction conditions. The catalysts used for the degradation are selective in the production of the liquid and gaseous products. Catalytic cracking has the advantage of leading to the high contents of products having higher commercial value [1, 2].

The polystyrene pyrolysis was investigated at a relative low temperature range of 370 to 400°C using a batch-type stirred vessel. The oil products were identified and determined by gas chromatography mass spectrometry (GC-MS) technique. The main products were single aromatic species (styrene ca. 70 wt.%, α-methylstyrene, toluene) and double aromatic species (1,3-diphenylpropane and 1,3-diphenylbutene) [3]. The study of polystyrene degradation was made by continuous distribution kinetics in a bubbling reactor. Molecular-weight distributions of products were determined by gel permeation chromatography and indicate the random and chain scission mechanism. The applied mathematics model accounts for the mass transfer of vaporized products from polymer melt to gas bubble [4]. The pyrolysis of polystyrene waste in a fluidized-bed reactor generated the residue that is an important factor in the recovery of styrene monomer and oil from polystyrene waste. The optimum temperature was found to be 550°C for the recovery of the maximum oil yields of 19-20%, styrene monomer of 10-11% and gas products by using of two types of ZSM-5 zeolites [5]. The catalytic transformation of polystyrene waste into hydrocarbons with higher commercial value was almost complete between 400-500°C by using H-ZSM-11 and Zn-ZSM-11 modified zeolites. Thus the authors obtained a quantity of liquid hydrocarbons greater than 94.96 wt% and a lower quantity of solid residues (<0.3 wt.%). The main liquid hydrocarbons of polystyrene degradation were 1,5-hexadiene and styrene, and in minor proportion indane and α-methylstyrene, these compounds being very important in the polymer technology and fine chemical field. The reaction products were analyzed by gas chromatography mass spectrometry [6]. The halloysite catalysts presented a good catalytic performance for the degradation of polystyrene. Styrene and ethylbenzene were the main components of liquid products obtained with the selectivity over 99% determined by GC-MS. The high selectivity to styrene was observed at higher temperatures. Acidity of catalysts, reaction temperature and contact time were necessary to control the product distribution between styrene monomer and ethylbenzene [7]. Pyrolysis of high-impact polystyrene over the zeolite Al-MCM-41 showed an important decomposition that depends on polymer/catalyst contact and it is observed by TGA in three steps. The results obtained showed the possibility of using TGA as a fast tool in order to characterize different styrene-butadiene copolymers [8]. The catalytic pyrolysis of polystyrene over base modified silicon mesoporous molecular sieve (K_2O/Si-MCM-41) was made at 400°C when the conversion of polystyrene was 90.53%, the yield of liquid products was 85% and the yield of styrene reached of 69.02%. The reaction products were analyzed by gas chromatography: GC-MS, GC-FID (flame ionization detector) [9]. The dealuminated HY zeolites were successfully applied for expandable polystyrene waste degradation in a batch operation at 375°C. The HY catalyst showed an increase in oil yield with a concomitant decrease in coke and residual products. The styrene monomer-to-styrene dimer ratio increases notable over steam-treated zeolite HY-700 and the conversion and product distribution depend on acidity of zeolites [10]. Catalytic degradation of polystyrene into liquid fuels has been carried out in a simple experimental set-up using Al_2O_3 supported Sn and Cd catalysts. The major component in liquid product was the aromatic hydrocarbon with at least 80% selectivity to ethylbenzene. The liquid product is suitable to be used as fuel with kerosene [11]. Styrene monomer recovery from polystyrene waste was studied in supercritical solvents by a novel fast process for to avoid coke formation. The highest yield of styrene obtained from polystyrene in supercritical toluene at 360°C for 20 min reached 77 wt.% [12]. Benzene was used as a solvent for the degradation of polystyrene waste in the presence of hydrogen at elevated temperature and pressure and of metal oxide catalysts. The most suitable catalyst for polystyrene degradation in hydrogen environment was found manganese dioxide, a catalyst with higher reactivity. The final product was analyzed by gas chromatography and it contains mainly methanol, benzene, and styrene monomer [13]. The co-pyrolysis of waste polystyrene with coal was investigated at high temperature obtained by microwave copper interaction. The obtained liquid products were the oily fraction and the aqueous fraction containing sulfide. The oily liquid product was analyzed using GC-MS and it was found that it contains mainly aromatic compounds in a narrow range [14].

In order to establish the characteristics of products obtained from plastic waste recycling, various analytical techniques are mentioned in literature, namely: gas chromatography, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, size exclusion chromatography, energy-dispersive X-ray fluorescence spectroscopy, thermal analysis, headspace solid-phase microextraction, pyrolysis-GC with mass spectrometry detection (Py-GC-MS) [15-18].

In this work, GC-MS and FTIR techniques have been used to investigate the liquid products obtained from the thermal and catalytic degradation of polystyrene waste (PS) using different types of solid catalysts (amphoteric, acidic, basic). The paper describes the effect of the catalysts with different textural properties and the effect of temperature over the degradation of polystyrene waste and its conversion into styrene monomer.

RESULTS AND DISCUSSION

The textural properties of the calcined catalysts were determined by nitrogen adsorption-desorption isotherms at 77 K. Firstly the catalysts were degassed under vacuum at 160ºC for 5 hours and then their surface area was determined by BET procedure. The external surface area and micropore volume were obtained applying the t-plot (de Boer) method. The total pore volume was measured at relative pressure $P \cdot P_0^{-1} = 0.99$ and it was obtained by the BJH (Barrett, Joyner, Halenda) desorption method.

In Table 1 are presented the structural parameters of the metal oxide catalysts used for thermal degradation of polystyrene waste.

Table 1. The structural parameters of metal oxide catalysts

Catalysts	**Specific surface area, BET[a], $m^2 g^{-1}$**	**Micropore area[b] $m^2 g^{-1}$**	**Micropore volume[b] $cm^3 g^{-1}$**	**Total pore area[c] $m^2 g^{-1}$**	**Total pore volume[c] $cm^3 g^{-1}$**	**Average pore diameter[c] nm**
SiO_2	205.69	57.56	0.00560	301.79	0.535	7.1
CuO/Al_2O_3	158.64	61.18	0.01040	251.77	0.473	7.5
Al_2O_3 a	92.26	12.64	0.00030	48.59	0.063	5.2
Al_2O_3 b	40.70	6.48	0.00020	34.76	0.053	6.1
CaO	4.85	1.46	0.00010	4.56	0.029	25.3

[a] BET method; [b] t-plot method; [c] BJH desorption method

The thermal degradation experiments were conducted at 350°C and 430°C respectively operating temperature in absence and in presence of the metal oxide catalysts. The obtained thermal degradation products were classified in three groups: liquid, gas and residue. As known, the thermal and catalytic degradation yield of polymers depends on many parameters such as: temperature, polymer and catalyst type, experimental reactor, residence time of volatiles in reactor etc. [1, 2]. The temperature and the catalyst play an important role in the distribution of compounds of the liquid products obtained. The temperature is increased gradually to produce a gradual melting of the polymer. The polystyrene bed temperature is considered the degradation temperature of polystyrene waste. In order to compare the effect of catalyst on the yield and distribution of end-products the textural properties of the catalysts were taken into consideration.

The obtained liquid products from the catalytic degradation of the polystyrene waste, at 380ºC and 430ºC respectively, have different colours due to the type of used catalyst and the degradation temperature as it is presented in Figure 1. The code of liquids is according to the used catalyst for PS degradation. For example: PS-SiO_2 is the liquid product obtained at the thermal degradation of polystyrene waste in the presence of silica gel catalyst or PS is the liquid product obtained at the thermal degradation of polystyrene waste in absence of the catalyst.

The yields of the obtained products at thermal and catalytic degradation of polystyrene waste, calculated according to the equation (1-3), are presented comparatively in Figure 2.

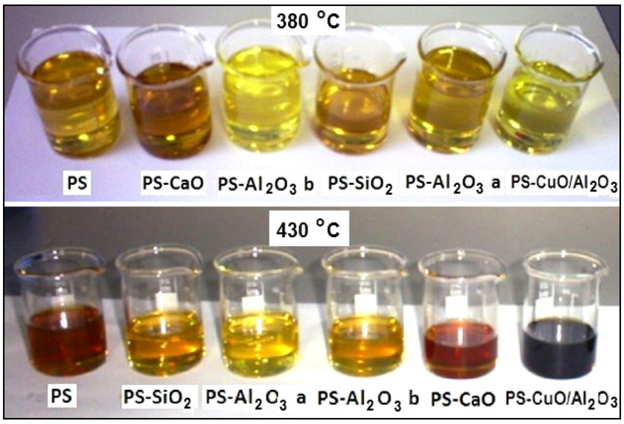

Figure 1. The liquid products obtained at the thermal and catalytic degradation of polystyrene waste.

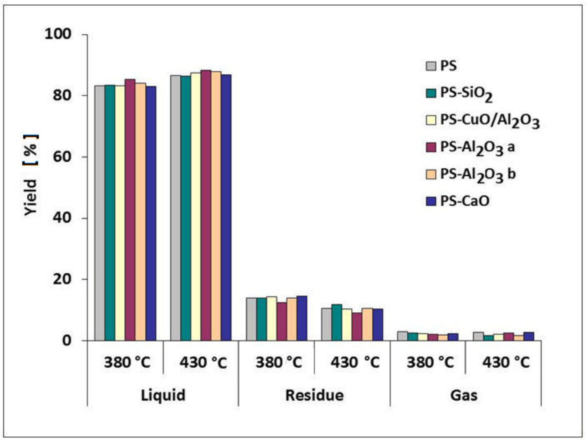

Figure 2. The yields of thermal degradation products of polystyrene waste in absence and in presence of catalysts.

The results presented in Figure 2 show that the yields of liquid products obtained by the thermal and catalytic degradation of the polystyrene waste have high values between 83 and 89%. The yield of liquids increases with increasing degradation temperature while the residue yield decreases with increasing temperature. Also, the yield of the obtained gaseous products has approximately equal values at both studied temperatures.

GC-MS Analysis

For the identification and quantification of hydrocarbons, the liquid products have been studied by GC-MS and by area percentage of TIC (total ion chromatogram). In Figure 3 are given the GC-MS chromatograms of all studied liquid products.

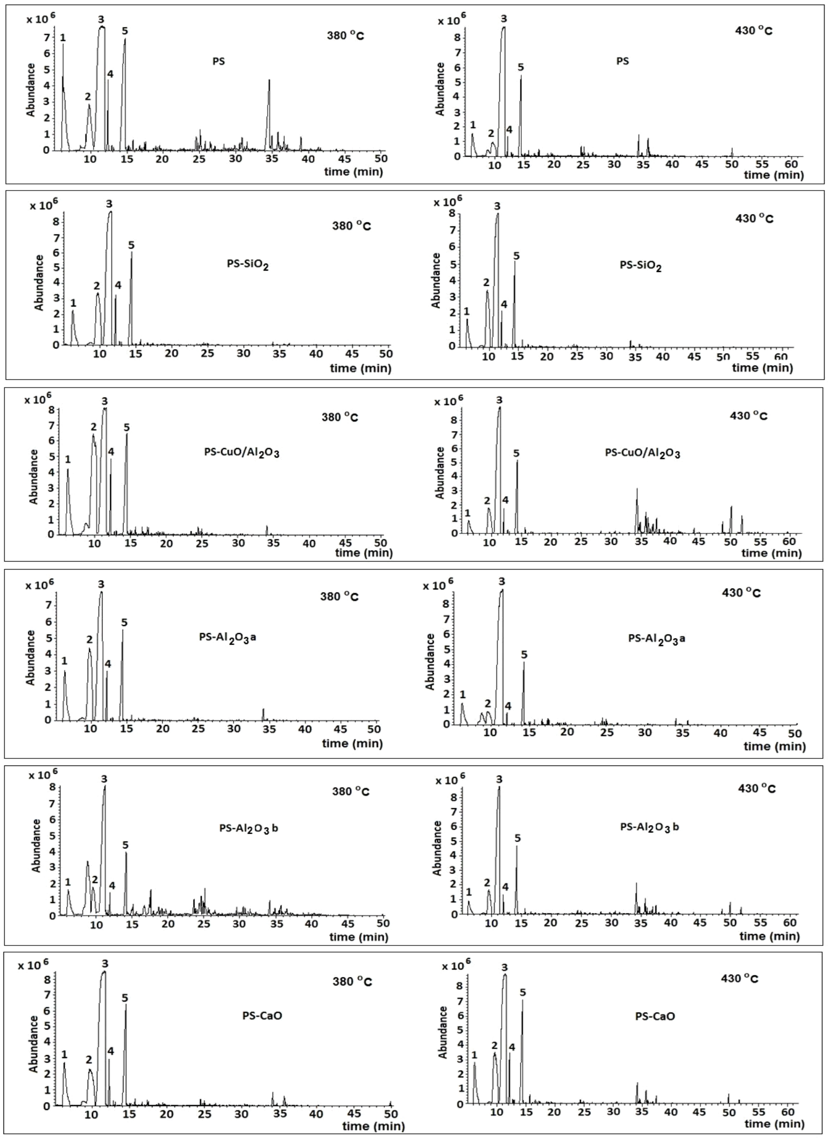

Figure 3. The GC-MS chromatograms of liquid products obtained by thermal and catalytic degradation of polystyrene waste.

The obtained liquids contain mainly the compounds: toluene (**1**, 6.28 min), ethylbenzene (**2**, 9.69 min), styrene monomer (**3**, 11.27 min) (up to 70%), 1-methylethylbenzene (**4**, 12.42 min) and α-methylstyrene (**5**, 14.40 min). In all cases, the styrene monomer is the major degradation product.

The compounds were identified by comparison of their mass spectra with those from the DATABASE/wiley6.1 spectra library. For example, in Figure 4 are shown the recorded mass spectra of the compounds (toluene, ethylbenzene, styrene monomer, α-methylstyrene) from the liquid products obtained from thermal degradation at 380°C of polystyrene waste in presence of alumina catalyst (Al_2O_3 a). For all studied liquids, the mass spectrum of each peak (compound) was compared with the corresponding mass spectrum from data spectra library.

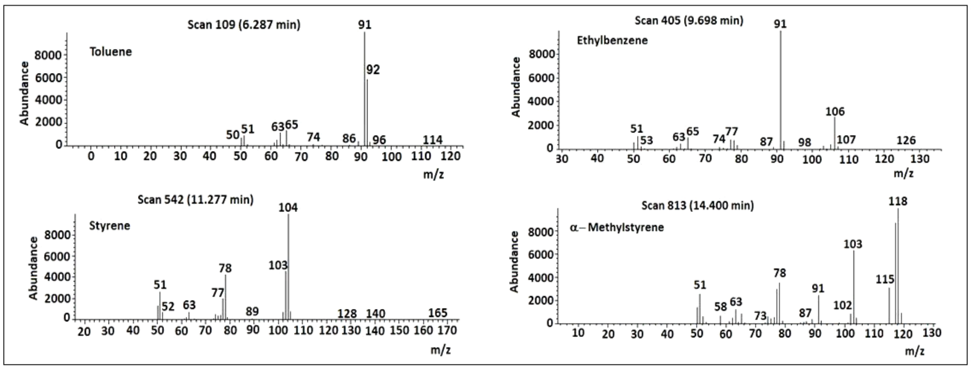

Figure 4. The mass spectra of compounds from liquid product obtained at thermal degradation at 380ºC of polystyrene waste in presence of alumina catalyst (Al_2O_3 a).

In the mass spectra from Figure 4 it can be observed the specific ions of each compound obtained by MS fragmentations: toluene (m/z 91, 92), ethylbenzene (m/z 91, 106), styrene monomer (m/z 78, 104), α-methylstyrene (m/z 78, 103, 118). These data certify the presence of these compounds in the liquid product.

Besides these main compounds of the studied liquid products, the GC-MS chromatograms contain some small peaks of other compounds found in smaller quantities. In some cases (PS at 380ºC, PS-CuO/Al_2O_3 at 430ºC or PS-Al_2O_3 b at 380ºC) the thermal degradation of polystyrene waste produces these secondary compounds like heptylbenzene (25.10 min) and 1,1'-(1,3-propanedil)*bis*-benzene (34.60 min). Their formation is desirable to be minimized by using the catalysts.

The GC-MS results of liquid products obtained from thermal and catalytic degradation of polystyrene waste are presented in Figure 5.

The results show that the temperature and the type of catalyst affect the quantity of the obtained styrene monomer. The largest quantities of the styrene monomer (68.76%, 380°C; 73.16%, 430°C) are obtained from thermal degradation of polystyrene waste in the presence of silica gel catalyst at both degradation temperatures. These results are due to the structural properties of the silica gel that is a solid acidic catalyst with a high BET specific surface area (205.69 $m^2 \cdot g^{-1}$) and a total pore area of 301.79 $m^2 \cdot g^{-1}$, respectively (Table 1).

The thermal degradation at 380°C of polystyrene waste in presence of CuO/Al_2O_3, a basic catalyst, produces the styrene monomer of 49.63% and a higher quantity of 21.38% ethylbenzene against the other cases. Instead, at 430°C is obtained a larger quantity of 67.68% styrene monomer.

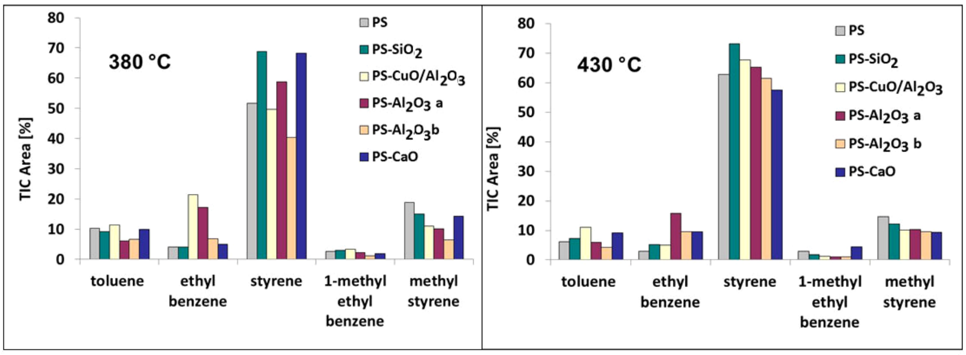

Figure 5. The distribution of compounds (TIC area, %) of liquid products obtained by the thermal and catalytic degradation of polystyrene waste.

The quantity of the styrene monomer obtained by the thermal degradation of polystyrene waste in presence of aluminas, amphoteric catalysts, is influenced by the structural properties and the temperature. The quantity of styrene monomer obtained using (Al_2O_3 a) catalyst with a higher BET specific surface area is greater than that obtained in the presence of (Al_2O_3 b) catalyst with a lower BET specific surface area.

The CaO is a basic solid catalyst with a low value for the BET specific surface area and the total pore volume, but with a high average pore diameter (Table 1). This type of catalyst produces a high quantity of styrene monomer at the temperature of 380°C as one can see in Figure 4.

We can conclude that the most efficient catalyst used in this thermal degradation method of polystyrene waste for both degradation temperatures is silica gel, an acid solid catalyst. Also, for the CaO, a basic solid catalyst it was obtained at 380°C a quantity of styrene monomer comparable with that obtained in presence of silica gel catalyst.

FTIR Analysis

Fourier-transform infrared spectrometry (FTIR) is able to quickly discern different bond vibration modes of a molecule. Thus, it is widely used to interpret the molecular characteristics and structure of compounds [20].

In Figure 6 are presented the FTIR spectra of the liquid product resulted from the thermal degradation of polystyrene waste in presence of SiO_2 at both temperatures. In all cases, the FTIR spectra of liquid products contain the same absorption bands. The main absorption bands and the type of the characteristic vibrations (stretching, bending, rocking) of the functional groups of the liquid products obtained from thermal and catalytic degradation of waste polystyrene are presented in Table 2.

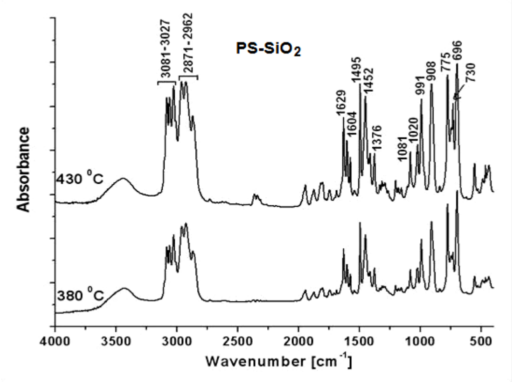

Figure 6. The FTIR spectra of obtained liquid fractions from thermal degradation of polystyrene waste in presence of SiO_2 catalyst.

Table 2. The assignments of absorption bands of studied liquid fractions [20]

Group frequency (cm^{-1})	Functional group	Assignment
3081,3060,3027	C-H aromatic ring	C-H stretching
2962	methyl	ν_{as} (CH_3), C-H asymmetric stretching
2925	methylene	ν_{as} (CH_2), C-H asymmetric stretching
2871	methyl	ν_s (CH_3), C-H symmetric stretching
1629	vinyl	ν (C=C), stretching (origin CH=CH)
1604,1495	aromatic ring	aromatic ring
1452	C-CH_3	δ_{as} C-CH_3 asymmetric bending
1376	methyl	C-H umbrella bending mode
1081, 1020	vinyl	C-H in plane bending
991, 908	vinyl	C-H out-of-plane bending
730	aromatic ring	aromatic ring rocking
775, 696	mono substituted aromatic ring	C-H out-of-plane bending of aromatic ring

In FTIR spectra of liquids products it can be observed three bands at 3081, 3060 and 3027 cm^{-1} that are assigned of the vibration of C-H bond in the aromatic ring. In addition, there are strong bands present in the region of 675–900 cm^{-1} that confirm the presence of aromatic compounds.

The presence of methyl groups are indicated by the bands from 2962 and 2871 cm^{-1} that correspond to the asymmetric and symmetric stretching vibrations of C-H bond. The band from 1376 cm^{-1} is assigned to umbrella bending mode vibration of C-H bond. The asymmetric stretching vibration of C-H bond in methylene group can be observed at 2925 cm^{-1}. The intense absorption band from 1629 cm^{-1} may be assigned to the characteristic vibrational mode of C=C bond (origin CH=CH), and those of 991 and 908 cm^{-1} are attributed to the C-H out-of-plane bending vibrations corresponding to the vinyl group. The bands at 1452 cm^{-1} can be assigned to asymmetric and symmetric bending vibration of C-CH_3 group. The aliphatic functional groups observed in the FTIR spectra indicate that these aliphatic groups are probably present as alkyl groups attached to the aromatic rings.

The FTIR results of the liquid product from the thermal and catalytic degradation of polystyrene waste are in good agreement with those obtained by GC-MS analysis of the liquid product.

CONCLUSIONS

Gas chromatography - mass spectrometry (GC-MS) and Fourier transform infrared spectrometry (FTIR) were used in this work to study the selectivity of different catalysts in the conversion of polystyrene waste into styrene monomer.

The thermal and catalytic degradation process of polystyrene waste have been performed at 380°C and 430°C, in absence and presence of five metallic oxide catalysts: amphoteric solids, two types of aluminas (Al_2O_3); acidic solid, silica gel (SiO_2); basic solids, calcium oxide (CaO) and copper oxide 13% deposited on alumina (CuO/Al_2O_3). The structural parameters of these catalysts influence the thermal degradation process of polystyrene waste by obtained products. Therefore, the yields of obtained liquid products have been calculated between 83.13% and 88.39% and these results depend on the experimental conditions, temperature and the type of catalysts.

The GC-MS results show that the obtained liquid products contain mainly toluene, ethylbenzene, styrene monomer (up to 73.16%), 1-methyl-ethylbenzene and α-methylstyrene. The silica gel, an acid solid catalyst has been founding the most efficient catalyst in this thermal degradation method of polystyrene waste at both degradation temperatures.

The FTIR spectra of liquid products of thermal and catalytic degradation of polystyrene waste show the presence of the functional groups methyl, methylene, aromatic ring and vinyl double bond and C-CH_3 bond from branched structure of the compounds from liquid products. All FTIR results are in good correlation with those obtained by GC-MS.

These techniques are very suitable for the characterization of liquid products obtained at the thermal and catalytic degradation of polystyrene waste and for the establishment of its further applications as feed stocks in chemical industry or for the obtaining of styrene monomer.

The results obtained show that the thermal degradation method of polystyrene waste in presence of silica gel catalyst can be used as recycling method of waste polystyrene into styrene monomer.

EXPERIMENTAL SECTION

Materials

For this study, polystyrene waste, namely vessel detergent boxes and disposable glass and plates, were used to study thermal and catalytic degradation into styrene monomer. These wastes were cut into small pieces (approximately 5 x 5 mm) and used as raw materials for the degradation process.

The metal oxide catalysts (Table 1) used for the degradation of polystyrene waste were two amphoteric solids (acidic and basic alumina, Al_2O_3), one acidic (silica gel, SiO_2), and two basic (calcium oxide, CaO; copper oxide 13% deposited on alumina, CuO/Al_2O_3) respectively. The aluminas (acidic alumina pH = 4.2, Al_2O_3 a; basic alumina pH = 9, Al_2O_3 b,) and the silica gel (SiO_2) used in this study are stationary phases for thin layer chromatography and have been produced at the *Raluca Ripan* Institute for Research in Chemistry Cluj-Napoca, Romania. Calcium oxide (CaO) was purchased from Fluka and copper oxide 13% deposited on alumina (CuO/Al_2O_3) as miniballs with a diameter of about 1 mm, from Aldrich.

The studied catalysts were subjected to a heating treatment in an oven in two stages: first at 200°C for 2 hours to remove the adsorbed water from the mesopores, then followed another heat treatment at 500ºC for 5 hours to activate the active centres.

After the thermal treatment the initial properties of alumina and silica gel have been modified. The pH values of both aluminas became 8.55. This can be explained by the removing of chlorine from the acidic alumina surface. These calcined aluminas are amphoteric solids with different textural properties and they were used as catalysts. Over 200°C, the thermal treatment of silica gel determine changes on its structure due to the removing of the water entrapped by hydrogen bonds from the hydroxyl groups of the surface [19].

The textural properties of the calcined catalysts were determined by nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics TriStar II 3020 instrument.

Thermal Degradation Procedure

Thermal degradation of the polystyrene waste was performed in a laboratory installation equipped with: glass vessel, heating mantle with thermostat, thermometer with thermocouple, condenser for cooling and condensing of the resulted gases, graduated cylinder to collect the liquid product and a special bag for the collection of the gaseous product. An amount of 30 g from polystyrene waste was subjected to the thermal degradation at operating temperature. The catalyst was added in the vessel in a mass ratio of 1/10 to the polystyrene waste. Before the starting of the polystyrene degradation procedure, the nitrogen was continuously passed through the installation with a flow rate of 30 mL min^{-1} for several minutes to eliminate the air. Then it was followed by the thermal decomposition step by increasing the temperature gradually up to 380°C and 430°C respectively, in order to produce a gradual melting of the polymer. The degradation temperature was considered the temperature of the polystyrene bed. The condensable gases were condensed in a water cooled condenser (4°C) and collected as a liquid product. The incondensable gases were collected in a special bag as a gaseous product. The small quantity of residue and the used catalyst remain in the glass vessel. The liquid product were measured and analysed by GC-MS and FTIR.

Analysis of Products

The yields of obtained products by PS thermal and catalytic degradation (L – liquid products, R – residue and G – gaseous products) were calculated using the equations 1-3. The liquid product and the residue were weighed directly.

$$L(wt.\%) = \frac{m_L}{M_{PS}} \cdot 100 \tag{1}$$

$$R(wt.\%) = \frac{m_R}{M_{PS}} \cdot 100 \tag{2}$$

$$G(wt.\%) = 100 - (L + R) \tag{3}$$

where m_L is the weight of liquid product (g), m_R the weight of residue (g) and M_{PS} the weight of polystyrene waste (g).

The liquid product was subjected to dehydration with $MgSO_4$ in order to remove any traces of water that can affect the GC-MS and FTIR analyses. GC-MS measurements were made using a Hewlett Packard HP 5890 Series II GC gas chromatograph interfaced to a Hewlett Packard 5972 Series mass selective detector with a DB-5MS capillary column (30 m x 0.53 mm ID x 1.50 μm film thickness). Temperature of the injector was 250°C. MS mode was carried out in full scan, with the scan range of 1.6-700 amu and the scan speed up to 1800 $\text{amu} \cdot \text{s}^{-1}$. The ionization intensity of 70 eV and the multiplier voltage of

1823.5 V were used. Oven temperature program was as follows: the initial temperature of 40°C was held for 4 min, increased with 5°C min^{-1} at 280°C and maintained at this final temperature for 10 min. The volume of injected sample was 1 μL. The acquisition of chromatographic data was performed by means of the HPchem software. All mass spectra were interpreted using the library spectra (DATABASE/wiley6.1).

The liquid product was measured also by spectrometric infrared technique with a JASCO-FTIR 610 Fourier-transform infrared spectrometer in the 4000-400 cm^{-1} wave number range, using the liquid film technique. The FTIR spectra of all the studied liquid products were registered at room temperature.

ACKNOWLEDGMENTS

This paper was supported by the project "Development and support of multidisciplinary postdoctoral programmes in major technical areas of national strategy of the Research-Development-Innovation" 4D-POSTDOC, contract no. POSDRU/89/1.5/S/ 52603, project co-funded by the European Social Fund through Sectoral Operational Programme Human Resources Development 2007-2013.

REFERENCES

1. K. Pielichowski, J. Njuguna, “Thermal Degradation of Polymeric Materials”, Rapra Technology Limited, Shawbury, **2005**.
2. T. Maharana, Y.S. Negi, B. Mohanty, *Polymer-Plastics Technology and Engineering*, **2007**, *46*, 729.
3. Y.S. Kim, G.C. Hwang, S.Y. Bae, S.C. Yi, S.K. Moon, H. Kumazawa, *Korean Journal of Chemical Engineering*, **1999**, *16*, 161.
4. W.S. Cha, S.B. Kim, B.J. McCoy, *Korean Journal of Chemical Engineering*, **2002**, *19*, 239.
5. C.G. Lee, J.S. Kim, P.S. Song, G.S. Choi, Y. Kang, M.J. Choi, *Korean Journal of Chemical Engineering*, **2003**, *20*, 133.
6. L.B. Pierella, S. Renzini, D. Cayuela, O.A. Anunziata, *2nd Mercosur Congress on Chemical Engineering; 4th Mercosur Congress on Process Systems Engineering*, **2005**, http://www.enpromer2005.eq.ufrj.br/lng/en.
7. J.W. Tae, B.S. Jang, J.R. Kim, I. Kim, D.W. Park, *Solid State Ionics*, **2004**, *172*, 129.
8. A. Marcilla, A. Gémez-Siurana, J.C. García Quesada, D. Berenguer, *Polymer Degradation and Stability,* **2007**, *92*, 1867.
9. C. Xie, F. Liu, S. Yu, F. Xie, L. Li, S. Zhang, J. Yang, *Catalysis Communications*, **2008**, *9*, 1132.

10. V.R. Chumbhale, J.S. Kim, W.Y. Lee, S.H. Song, S.B. Lee, M.J. Choi, *Journal of Industrial and Engineering Chemistry*, **2005**, *11*, 253.
11. A. Ramli, D.R. Abu Bakar, *Journal of Applied Sciences*, **2011**, *11*, 1346.
12. K. Huang, L. Tang, Z. Zhu, C. Zhang, *Polymer Degradation and Stability,* **2005**, *89*, 312.
13. P. Tivary, C. Guria, *Journal of Polymer and the Environment*, **2010**, *18*, 298.
14. Z. Hussain, K.M. Khan, N. Basheer, K. Hussain, *Journal of Analytical and Applied Pyrolysis,* **2011**, *90*, 53.
15. F. Vilaplana, A. Ribes-Greus, S. Karlsson, *Analytica Chimica Acta*, **2007**, *604*, 18.
16. N. Miskolczi, L. Bartha, *Journal of Biochemical and Biophysical Methods,* **2008**, *70*, 1247.
17. P. Kusch, G. Knupp, *Journal of Polymer and the Environment,* **2004**, *12*, 83-87.
18. R. Rial-Otero, M. Galesio, J.L. Capelo, J. Simal-Gándara, *Chromatographia*, **2009**, *70*, 339.
19. Y. Sander González, C. Costa, C.M. Márquez, P. Ramos, *Journal of Hazardous Materials,* **2011**, *187*, 101.
20. B.C. Smith, “Infrared Spectral Interpretation. A Systematic Approach”, CRC Press, Boca Raton, **1999**.