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Degradation of polystyrene waste over base promoted Fe catalysts[☆]

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Abstract

One of the most attractive processes is the catalytic degradation of polystyrene (PS). This process enables to get styrene monomer (SM) at relatively low temperature with a high selectivity. In this study, the modified Fe-based catalysts were employed for the catalytic degradation of EPSW (expandable PS waste), where carboanion may lead to high selectivity of SM in the catalytic degradation of PS. The yield of oil (Y_{Oil}) and SM (Y_{SM}) were increased in the presence of Fe-based catalysts and with increasing reaction temperature. Y_{Oil} and Y_{SM} were obtained over Fe–K/Al_2O_3 at the relative low reaction temperature (400 °C) 92.2 and 65.8 wt.%, respectively. The value of E_a (activation energy) is obtained as 194 kJ/mol for the thermal degradation of EPSW. However, the E_a was decreased considerably from 194 to 138 kJ/mol in the presence of the catalysts (Fe–K/Al_2O_3).

Keywords: Catalyst; Degradation; Kinetics; Polystyrene waste

1. Introduction

Recycling of waste plastics has been of great interest in terms of environment solution and economic feasibility during the last 10 years. Municipal and industrial plastic wastes are predominantly by landfill, incineration and true material recycling. Each of these methods has disadvantages. Landfill and incineration of plastic waste are less desirable due to high cost, poor biodegradability and the possibility of unacceptable emission. Also, material recycling generally is not accepted as a long-term solution. Consequently, tertiary recycling such as thermal or chemical recycling is more attractive for the energy or chemical recovery [1–3]. Generally it is said that thermal recycling of plastics such as polyethylene (PE) or polypropylene (PP) to get oils is invalid method than chemical recycling method due to the low price of crude oil. However, polystyrene (PS) can be depolymerized at relatively low temperature to obtain the styrene monomer (SM) with a high selectivity in contrast with PE and PP, making up around 10 wt.% of the total plastic stream [3,4].

Advanced reactors enhancing heat transfer has been developed to increase the yield of SM by thermal degradation of PS [5–7], the yield of SM reached 78 wt.% in the fluidized bed reactors at 600 °C [6]. On the other hand, heat mediums such as medium particles (ceramic ball), heavy oils (mineral oil, bean oil) and solvents (benzene (BZ), toluene (TOL), cyclohexane) were used in the direct thermal degradation to prevent limitations of heat and mass transfer [8–10].

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Catalytic degradation of waste plastics has been studied to solve the problems associated with thermal degradation by controlling the propagating species and activation energy, get the desired products at lower reaction temperature. One of the most attractive processes is the catalytic degradation of PS, to produce SM at relatively low temperature with a high selectivity. Subsequently SM can be recycled to new PS [11–13].

Most studies of catalytic degradation of PS have been investigated using solid acid catalysts, which are well known for their ability to cleave C–C bonds in the petroleum industry [2–4,14]. However, relatively few studies have been performed using solid base and transition metal catalysts. Zhang et al. [15] reported 70 wt.% yield of SM by PS degradation over a highly basic catalyst BaO where carboanion intermediate lead degradation to SM rather than carbocation or carboradical intermediates [15,16]. If the proposed mechanism is correct, conversion (reduction) of thermally degraded carboradical to carboanion may also lead to high selectivity of SM in the catalytic degradation of PS.

From the previous work we have shown that Fe-based catalysts are suitable for the reduction of carbon oxides by hydrogenation route [17,18]. To explore our knowledge in the degradation of PS to SM by way of abstraction of H radical towards reduction of carboradical into carboanion we have undertaken the present work.

In the present study, we are reporting the results of our experiments carried over Al_2O_3, Fe_2O_3 and modified Fe/Al_2O_3 with Ba, K, Zn and Mg as the promoters aiming at improvement in Y_{Oil} and Y_{SM}. In addition, the activation energy (E_a) of catalytic and thermal degradation calculated by Arrhenius plot from the experimental results is compared with E_a as calculated from thermogravimetric analysis (TGA).

Table 1
Property of catalysts

Catalyst	Composition (wt.%)	S_{BET} (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
Fe/Al_2O_3	20:100	128.5	95.2	0.31
$Fe–K/Al_2O_3$	20:10:100	154.6	96.2	0.35
$Fe–Ba/Al_2O_3$	20:10:100	152.8	95.4	0.36
$Fe–Zn/Al_2O_3$	20:10:100	100.8	115.9	0.29
$Fe–Mg/Al_2O_3$	20:10:100	138.4	98.1	0.34

2. Experimental

2.1. Catalysts preparation and materials

Alumina was used as a catalyst and support material (γ-alumina, Strem Co.) and ferric oxide was used as a transition metal (Fe_2O_3, Shinyo Chemicals Co.). The Fe, K, Ba, Zn and Mg coated catalysts were prepared by impregnating aqueous solutions of $Fe(NO_3)_3{\cdot}9H_2O$, K_2CO_3, $Ba(NO_3)_2$, $Zn(NO_3)_3{\cdot}6H_2O$, $Mg(NO_3)_3$. The catalysts were dried (110 °C, 24 h), calcined (500 °C, 12 h) and crushed ($d_p = 45–75\,\mu m$). The composition and properties of the catalysts are summarized in Table 1. PS materials were used EPSW (expanded PS waste) from agricultural and marine market, which were crushed and sieved in the range of 1–2 mm diameter. Analysis of EPSW is shown in Table 2.

2.2. Apparatus and procedure

Experiments were carried out in a batch stirred tank reactor (0.08 m ID × 0.12 m H) made of pyrex glass, depicted in Fig. 1. EPSW (100 g) and 1 g of catalyst were fed to the reactor. The dried and filtered nitrogen was injected continuously into the reactor from gas cylinder. The gas flow rate was maintained

Table 2
Analysis of EPSW

Feed material	Element (wt.%)					GPC[a]	
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	M_w	M_n
EPSW	89.56	7.83	0.02	0.00	0.95	219000	100100

[a] Average molecular weight (M_w) and number of average molecular weight (M_n) were measured by gel permeation chromatography (GPC).

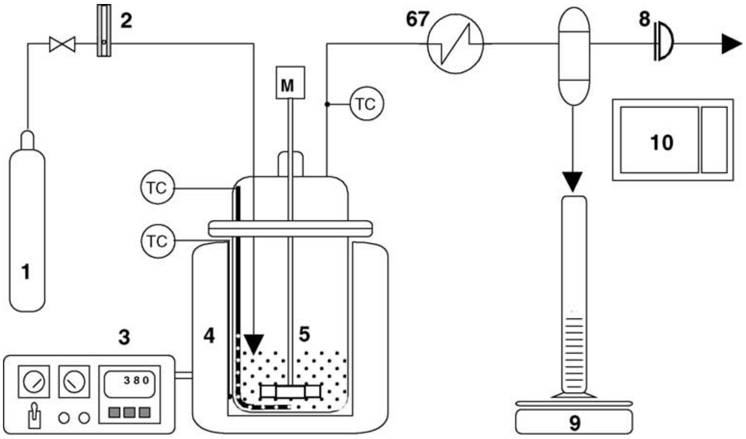

Fig. 1. Experimental apparatus: (1) N_2 gas cylinder; (2) flowmeter; (3) temperature controller; (4) heating mantle; (5) stirred tank reactor; (6) heat exchanger; (7) condenser; (8) wet gas meter; (9) balance; (10) GC.

at 50 ml/min with the aid of metering valve and flowmeter. The products of EPSW degradation were introduced into a heat exchanger and separated gas and liquid oils in the condenser. The temperatures at the heater surface and the reactor were measured by the iron constantan thermocouples (K-type), kept were along the wall of the reactor and were controlled by PID temperature controller at a heating rate of 10 °C/min. When the reaction temperature was reached at 300 °C, the stirrer was started at the speed of 200 rpm.

2.3. Analyses

The kinetics of EPSW degradation at non-isothermal condition was investigated using TGA (TA Instrument Co.) at various heating rates in the range of 10–50 °C/min in nitrogen atmosphere. The specific surface area, pore size and volume of the catalysts were measured by the BET apparatus (Micrometrics ASAP 2010).

The liquid products of the reaction were analyzed by a gas chromatograph (DS 6200) employing FID detector using BP-1 column. The gaseous products were analyzed on FID and TCD using poraplot-Q and carbosphere columns, respectively. The products were further confirmed by GC–MS (HP-5890 plus).

The amount of residue was weighed, which is the carbonaceous compounds remaining in the reactor. The coke deposit on the reactor and the catalyst was calculated by measuring the solid materials after extraction of residue using BZ as a solvent and filtration of extract carried out. The amount of gaseous products was calculated by subtracting the sum of weights for liquid, residues and catalyst with coke from the total weight of EPSW sample and catalyst initially loaded to the reactor, exception of inorganic and metallic impurities (Table 2).

The yield of oil product (Y_{Oil}) and SM (Y_{SM}) were determined by the following equations:

$$\text{Yield of oil}: \quad Y_{\mathrm{Oil}} = \frac{W_{\mathrm{o}}}{W_{\mathrm{f}}} \times 100 \tag{1}$$

$$\text{Yield of styrene monomer}: \quad Y_{\mathrm{SM}} = \frac{W_{\mathrm{SM}}}{W_{\mathrm{f}}} \times 100 = \frac{W_{\mathrm{SM}} \times Y_{\mathrm{Oil}}}{W_{\mathrm{o}}} \times 100 \tag{2}$$

where W_{o}, W_{SM} and W_{f} are the weight of obtained oil, the weight of feed material (EPSW) and the weight of obtained SM, respectively.

3. Kinetic theory

In the kinetics of EPSW degradation, it is common to use the basic rate equation of conversion α:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^{n} \tag{3}$$

where n is the order of reaction and k the specific rate constant. The temperature dependence of k is expressed by Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A, E, T and R are the pre-exponential factor, the activation energy (J/mol), the temperature of reaction (K), and the gas constant (8.314 J/mol K), respectively. From Eq. (4), the activation energy in the stirred tank reactor is calculated as a first order reaction.

In the kinetic data using TG analyzer, also it is based on Kissinger's method for thermal degradation. Kissinger's method for calculating the kinetic parameters uses the temperature at which the rate of mass loss is the highest (T_m) and is shown by the equation:

$$\frac{E_a \beta}{RT_m^2} = An(1-\alpha_m)^{n-1} \exp\left(\frac{-E_a}{RT_m}\right) \quad (5)$$

where β is the heating rate ($\beta = dT/dt$) and T_m and α_m the maximum degradation rate temperature and weight loss fraction, respectively. It is assumed that the degradation is first order and that conversion does not depend on heating rate. Apparent activation energies are determined from the parameters of the straight line obtained by drawing the dependence $\ln(\beta/T_m^2)$ vs. $1/T_m$ [19].

4. Results and discussion

4.1. Catalysts activity

Catalytic performance as a function of time-on-stream carried out in the batch stirred tank reactor is depicted in Fig. 2. In the direct thermal degradation of EPSW (expandable PS waste), the yields of liquids products (Y_{Oil}) was obtained only 56 wt.% at 375 °C for 90 min. However, Y_{Oil} was higher in the catalytic degradation than that of thermal at the identical experimental conditions for the same period of time. This behavior may be attributed to an increase in the rate of degradation occurs in the presence of the catalyst (Al_2O_3, Fe_2O_3 and Fe/Al_2O_3). It may be noted that

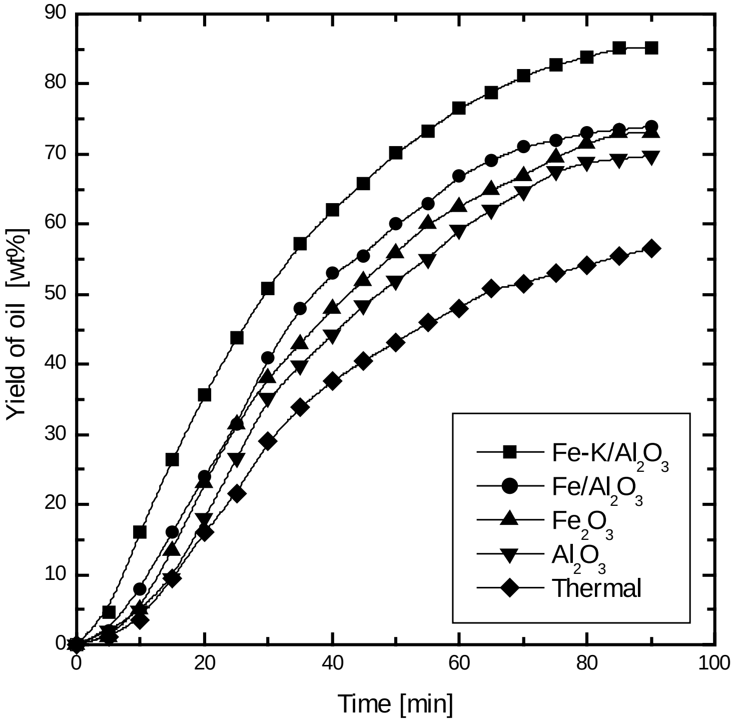

Fig. 2. Yield of oil as a function of time ($T = 375$ °C).

Y_{Oil} is higher over Fe_2O_3 than Al_2O_3. It can be understood that solid acid catalysts such as silica, alumina and HZSM-5 is more easily deactivated than transition metal oxides due to coke formation although strong acid sites on the catalyst surfaces have the potential to disrupt C–C bonds in the waste plastics. While transition metal oxides inducing radical (redox) reaction enable to accelerate EPSW degradation and prevent deactivation which could be attributed to many base sites on their surfaces [15].

The modified Fe–K/Al_2O_3 shows relatively excellent catalytic performance as compared to Al_2O_3, Fe_2O_3 and Fe/Al_2O_3 catalysts. Y_{Oil} was reached 85 wt.% over Fe–K/Al_2O_3 due to the well-dispersed base promoter. It has been observed that the high dispersion of Fe and K on Al_2O_3 support provide strong basicity (higher CO_2 uptake) as well as relatively high surface area of active phases [17]. The higher yields of styrene from PS may ascribe to the stronger base sites on the surface of the solid basic catalyst like Fe–K/Al_2O_3. Hence it seems acceptable to think that the styrene yield obtained over the catalyst studied is in accordance with the earlier work [15].

Table 3 depicts the comparison of different promoters (K, Ba, Zn and Mg oxides) for their catalytic performance in the degradation of EPSW. Relatively enhanced catalytic activity was obtained with K or Ba promoted Fe-based catalysts in terms of the Y_{Oil} and Y_{SM}. In all cases, main product was liquid oil and the major component of liquid products was SM, and others observed were toluene (TOL), ethylbenzene (EB), α-methylstyrene (α-MS), 1,3-diphenylpropane (DPP) and 2,4-diphenylbutene (DPB), isopropylbenzene (IPB), benzene (BZ). Other byproducts observed were the gaseous products such as methane, ethylene and propylene, the residual products such as DPP and other diphenyls, triphenyls and the cokes (Table 3).

Fig. 3 indicates the comparison of oil product distribution between catalytic and thermal degradation of EPSW. The selectivities to various liquid products changed considerably with increasing degradation conversion. The selectivity of SM was decreased with increasing the degradation conversion for as well. However, the selectivities of EB, α-MS and TOL were increased with increasing conversion level. This can be attributed to the higher reaction time, the further degradation brings such as thermal and catalytic cracking. It is interesting to note that catalytic degradation of EPSW over Fe–K/Al_2O_3 was maintained at higher SM selectivity with increasing conversion. The SM selectivity was also higher in catalytic degradation.

Zhang et al. [15,16] proposed that the thermal degradation of PS starts with random initiation to form polymer radicals, while the catalytic degradation of PS

Table 3
Product distribution in the degradation of EPSW over various catalysts[a]

	Catalyst							
	Thermal	Al_2O_3	Fe_2O_3	Fe/Al_2O_3	Fe–K/Al_2O_3	Fe–Ba/Al_2O_3	Fe–Zn/Al_2O_3	Fe–Mg/Al_2O_3
Y_{Oil}	56.5	69.8	73.0	74.0	85.1	83.8	82.7	77.1
Y_{RES}	37.9	22.7	21.0	19.0	9.5	10.3	10.6	18.3
Y_{COKE}	0.6	2.3	1.2	1.1	0.8	1.2	0.9	0.8
Y_{GAS}	5.0	5.2	4.8	5.9	4.6	4.7	5.8	3.8
Product composition								
BZ	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
TOL	8.6	10.1	5.7	5.6	5.7	4.3	5.2	7.3
EB	5.5	5.3	3.1	3.0	2.3	2.8	3.1	4.2
SM	63.6	67.3	68.4	69.2	71.8	71.4	67.8	68.9
IPB	0.8	0.6	0.2	0.2	0.2	0.2	0.3	0.5
α-MS	12.0	8.7	6.9	5.9	7.7	5.7	7.6	11.2
DPP	2.4	1.0	3.7	3.9	2.4	2.8	3.9	1.7
DPB	1.7	0.4	5.9	6.7	4.2	6.2	3.7	0.8
Others	5.3	6.4	5.8	5.5	5.6	6.5	8.2	5.3

[a] $T = 375\,^{\circ}\mathrm{C}$. BZ: benzene; TOL: toluene; SM: styrene monomer; IPB: isopropylbenzene; α-MS: α-methylstyrene; DPP: 1,3-diphenylpropane; DBP: 2,4-diphenylbutene.

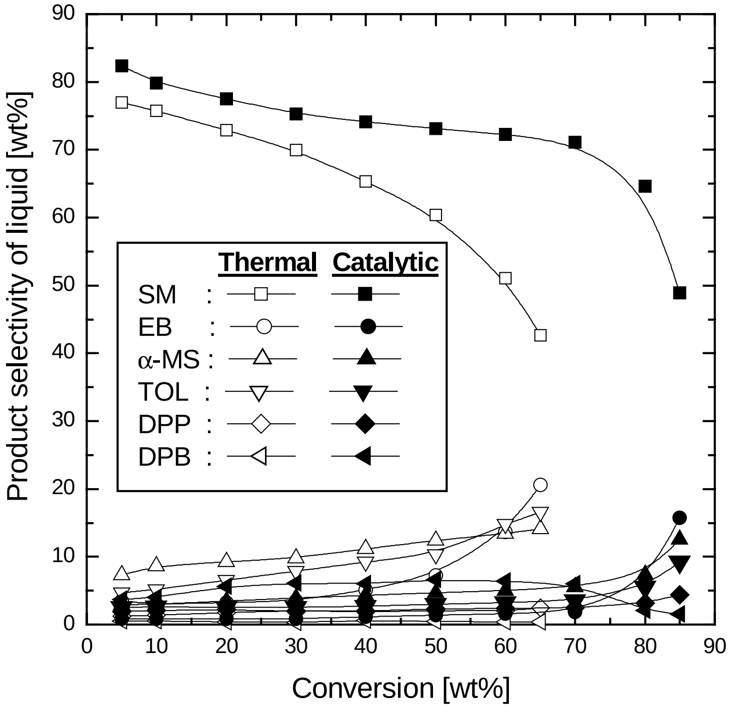

Fig. 3. Comparison of product selectivity by thermal and catalytic degradation (catalyst = Fe–K/Al$_2$O$_3$, T = 375 °C).

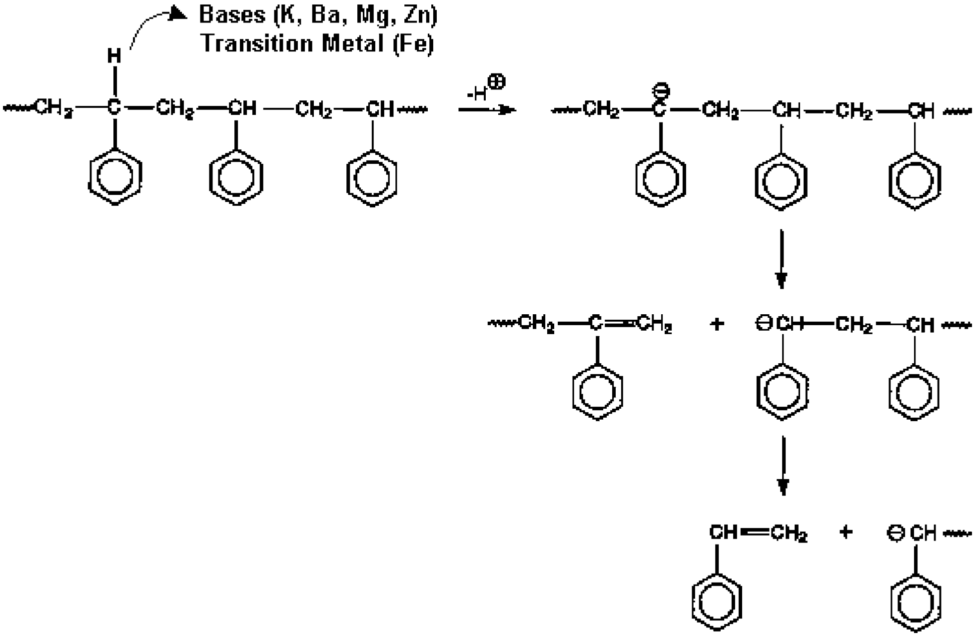

Fig. 4. Mechanism for the initiation and depolymerization of PS in the base promoted Fe catalysts.

over a highly basic BaO catalyst initiates by carboanion intermediate leading to degradation of PS to SM instead of the possibility of carbocation or carboradical intermediates. In the case of the transition metal catalyst such as iron oxides, reduction of thermally degraded carboradical to carboanion may also lead to high selectivity of SM in the catalytic degradation of PS. The proposed mechanism over base and transition metal catalyst is shown in Fig. 4.

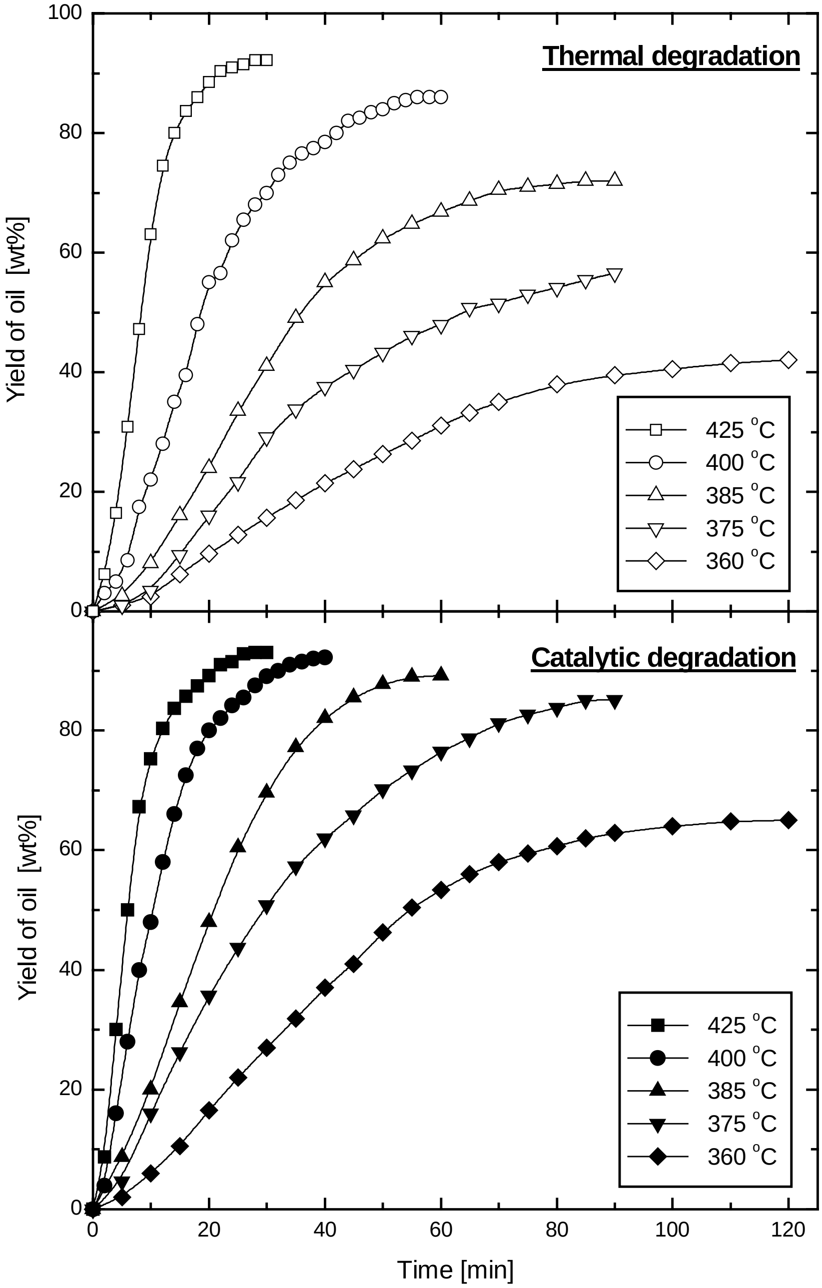

Fig. 5. Effects of reaction temperature on the yield of oil in the degradation of EPSW (catalyst = Fe–K/Al_2O_3).

4.2. Reaction temperature

Effects of reaction temperature on the Y_{Oil} are shown in Fig. 5. The Y_{Oil} is increased rapidly at relatively higher degradation temperature in the range of 360–425 °C. The values of Y_{Oil} are obtained as 41.7, 56.5, 72.0, 86.0 and 92.2 wt.% in the thermal degradation at 360, 375, 385, 400 and 425 °C, respectively. However, Y_{Oil} values are reached at 65.0, 85.1, 89.2, 90.2 and 93.0 wt.% in the catalytic degradation at the same temperatures.

Table 4 shows the product distribution in the catalytic degradation of EPSW at different temperatures. The Y_{Oil} were increased considerably with increasing temperature. Consequently, the yield of SM was increased although the SM selectivity was decreased with increasing temperature. The coke deposited on the surface of reactor and catalyst was increased insignificantly with rise in temperature. In this study, therefore, optimum reaction temperature can be considered a relatively high temperature (around 400 °C).

4.3. Kinetics

For the evaluation of catalytic degradation of EPSW in the batch stirred tank reactor, kinetic studies on the thermal and catalytic degradation were carried out using the experimental results from Fig. 5. The activation energy (E_a) of the thermal degradation was reevaluated with those obtained by TGA without catalyst charge. Typical TG curves of EPSW at various heating rates are shown in Fig. 6. Thermal degradation of EPSW was observed in the range of 350–475 °C and rapidly decomposed around 400 °C.

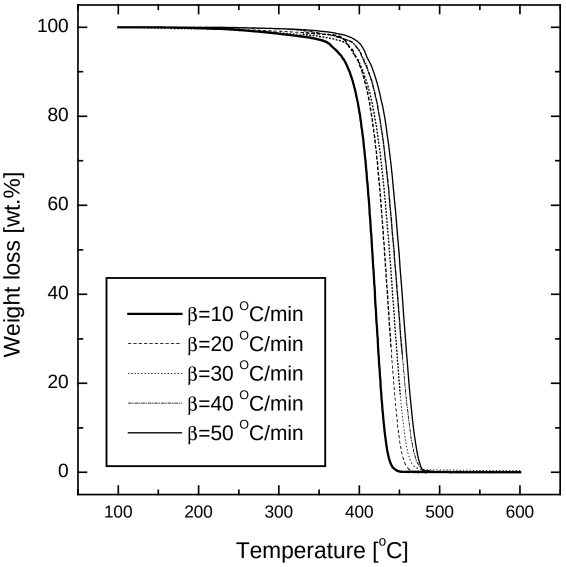

Fig. 6. Typical TG curves for the degradation of EPSW.

Table 4
Product distribution in the degradation of EPSW at different temperatures[a]

	Temperature (°C)				
	360	375	385	400	425
Y_{Oil}	65.0	85.1	89.2	92.2	93.0
Y_{RED}	30.2	9.5	6.0	2.6	1.4
Y_{COKE}	0.5	0.8	1.0	1.6	2.1
Y_{GAS}	4.3	4.6	3.8	2.6	3.5
Product composition					
BZ	0.1	0.1	0.1	0.1	0.2
TOL	4.9	5.7	5.4	6.2	5.5
EB	3.4	2.3	2.1	2.0	1.8
SM	72.9	71.8	71.8	71.4	70.3
IPB	0.3	0.2	0.4	0.4	0.4
α-MS	6.8	7.7	8.2	8.4	8.5
DPP	1.2	2.4	2.9	3.8	6.5
DPB	1.8	4.2	2.8	2.3	2.2
Others	8.7	5.6	6.3	5.4	4.6

[a] Catalyst = $Fe–K/Al_2O_3$. BZ: benzene; TOL: toluene; SM: styrene monomer; IPB: isopropylbenzene; α-MS: α-methylstyrene; DPP: 1,3-diphenylpropane; DPB: 2,4-diphenylbutene.

Fig. 7 shows the plot of $\ln(\beta/T_m^2)$ vs. $1/T_{\max}$ (Kissinger's method) using the TG and the plot of $\ln(k)$ vs. $1/T$ (Arrhenius plot) using the experimental. From the straight line, the E_a of thermal and catalytic degradation of EPSW were calculated and found to be 194 and 138 kJ/mol, respectively.

The kinetics for the degradation of PS has been reported by many researchers [3,11,20–22]. The differences between the activation energies reported by various studies can be attributed to differences in properties (molecular weight, presence of weak links, additives) of PS and in experimental conditions. In this study, the activation energies of thermal degradation of EPSW using the results of TGA and experiment have the identical value (194 kJ/mol). It is possible to select specific conversion range of 20–50 wt.% for comparison of E_a. These activation energies of thermal and catalytic degradation were comparable with other reported values as shown Table 5. The values

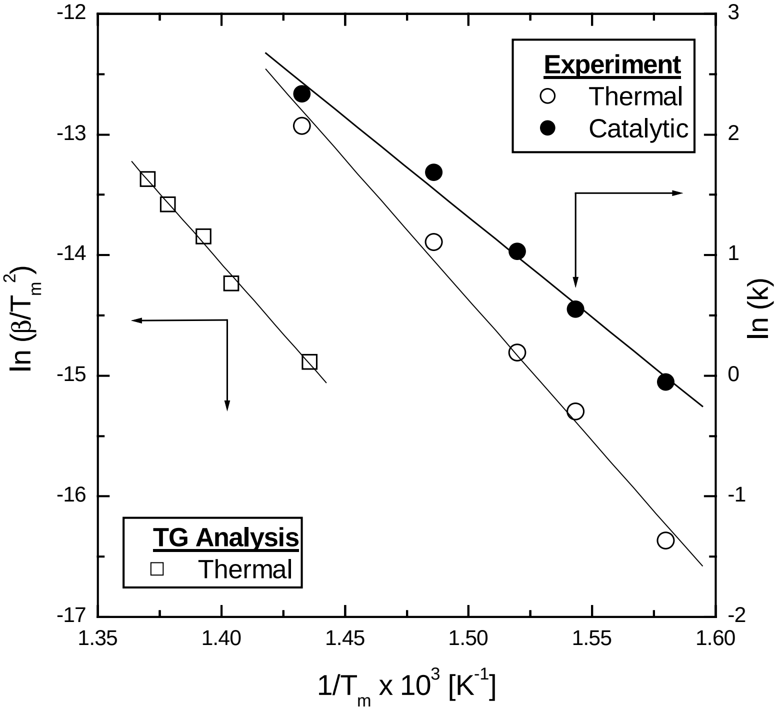

Fig. 7. Kinetics for the thermal and catalytic degradation of EPSW.

Table 5
Kinetics reported in the literature for the degradation of PS

Author	Condition	T (°C)	ξ (wt.%)	E_a (kJ/mol)
Anderson and Freeman [20]	Thermal	246–430	15–95	231–273
Westerhout et al. [21]	Thermal	365–400	70–90	204
Simard et al. [11]	Thermal	365–395	–	165.5
Carniti et al. [22]	Thermal	360–420	–	185
Carniti et al. [22]	MgO–Si	360–420	–	173
Lee et al. [3]	Thermal	350–425	–	380
Lee et al. [3]	Zeolite	350–425	–	360
Present study	TG-thermal	420–450	–	194
Present study	Exp.-thermal	360–425	20–50	194
Present study	Exp.-Fe–K/Al_2O_3	360–425	20–50	138

of E_a obtained by thermal and catalytic degradation of EPSW are in the agreement with those reported [21,22].

5. Conclusions

The application of modified Fe-based catalyst (Fe–K/Al_2O_3) for the catalytic degradation of EPSW, significantly improve Y_{SM} as well as Y_{Oil} at the relative low reaction temperature. It is observed that the nature of the base promoted Fe catalysts and reaction temperature (375–425 °C) play predominant role towards Y_{SM} and Y_{Oil}, respectively. The value of $E_a = 194$ kJ/mol is obtained for the thermal degradation of EPSW. However, the E_a was decreased considerably from 194 to 138 kJ/mol in the presence of the catalysts in the same conversion range (20–50 wt.%) for the catalytic degradation of PS.

Acknowledgements

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References

[1] H.S. Joo, J.A. Guin, Energy Fuel 11 (1997) 586.
[2] S. Ali, A.A. Garforth, D.H. Harris, D.J. Rawlence, Y. Uemichi, Catal. Today 75 (2002) 247.
[3] S.Y. Lee, J.H. Yoon, J.R. Kim, D.W. Park, Polym. Degrad. Stab. 74 (2001) 297.
[4] D.P. Serrano, J. Aguado, J.M. Escola, Appl. Catal. B 25 (2000) 181.
[5] W. Kaminsky, Makromol. Chem. Macromol. Symp. 48/49 (1991) 381.
[6] Y. Liu, J. Qian, J. Wang, Fuel Process. Technol. 63 (2000) 45.
[7] J.S. Kim, S.J. Kim, J.S. Yun, Y. Kang, M.J. Choi, Hwahak Konghak 39 (2001) 465.
[8] T. Masuda, T. Kushino, T. Matsuda, S.R. Mukai, K. Hashimoto, S. Yoshida, Chem. Eng. J. 82 (2001) 173.
[9] A. Karaduman, E.H. Simsek, B. Cicek, A.Y. Bilgesu, J. Anal. Appl. Pyrol. 62 (2002) 273.
[10] D. Dong, S. Tasaka, N. Inagaki, Polym. Degrad. Stab. 72 (2001) 345.
[11] Y.D.M. Simard, M.R. Kamal, D.G. Cooper, J. Appl. Polym. Sci. 29 (1985) 843.
[12] T. Faravelli, M. Pinciroli, F. Pisano, G. Bozzano, M. Dente, E. Ranzi, J. Anal. Appl. Pyrol. 60 (2001) 103.
[13] S. Ide, H. Nanbu, T. Kuroki, T. Ikemura, J. Appl. Polym. Sci. 29 (1984) 2561.
[14] G. de la Puente, J.M. Arandes, U.A. Sedran, Ind. Eng. Chem. Res. 36 (1997) 4530.
[15] Z. Zhang, T. Hirose, S. Nishio, Y. Morioka, N. Azuma, A. Ueno, H. Ohkita, M. Okada, Ind. Eng. Chem. Res. 34 (1995) 4514.
[16] O.S. Woo, N. Ayala, L. Broadbelt, Catal. Today 55 (2000) 161.
[17] P.H. Choi, K.W. Jun, S.J. Lee, M.J. Choi, K.W. Lee, Catal. Lett. 40 (1996) 115.
[18] M.J. Choi, J.S. Kim, H.K. Kim, Y. Kang, S.B. Lee, K.W. Lee, Kor. J. Chem. Eng. 18 (2001) 646.
[19] B. Andričić, T. Kovačić, Polym. Degrad. Stab. 65 (1999) 59.
[20] D.A. Anderson, E.S. Freeman, J. Polym. Sci. 54 (1961) 253.
[21] R.W.J. Westerhout, J. Waanders, J.A.M. Kuipers, W.P.M. van Swaaij, Ind. Eng. Chem. Res. 36 (1997) 1955.
[22] P. Carniti, A. Gervasini, S. Bernardelli, Polym. Degrad. Stab. 57 (1997) 301.