

## Supporting Information

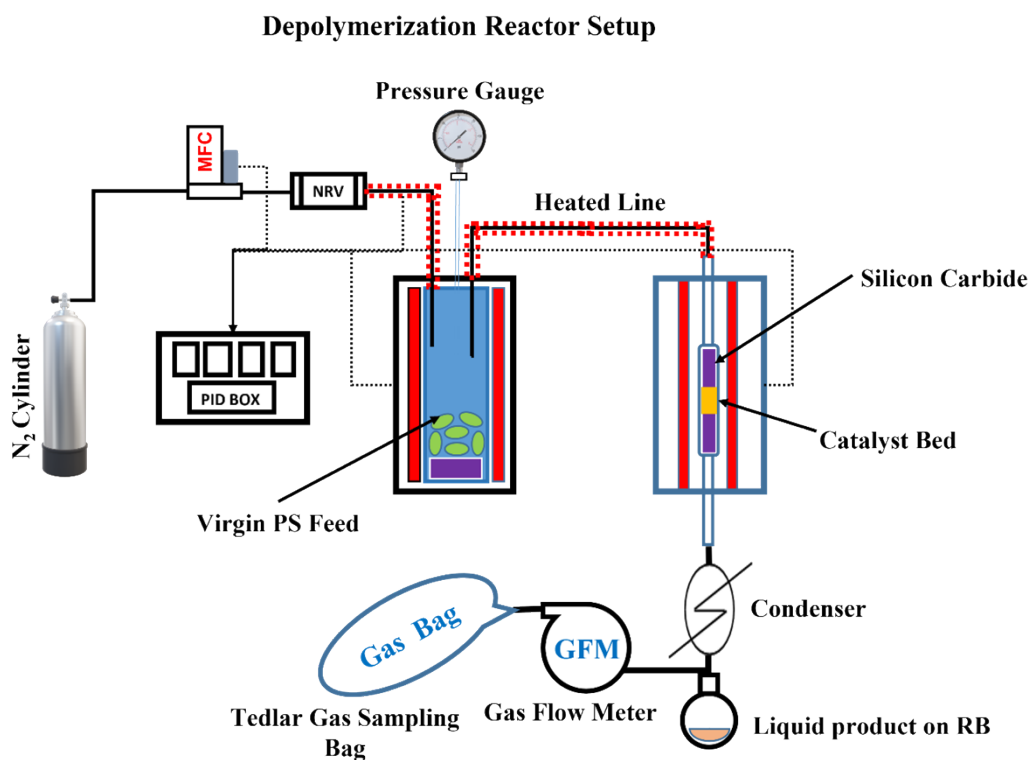
### Sustainable Production of Styrene from Catalytic Recycling of Polystyrene over Potassium Promoted Fe-Al<sub>2</sub>O<sub>3</sub> Catalyst

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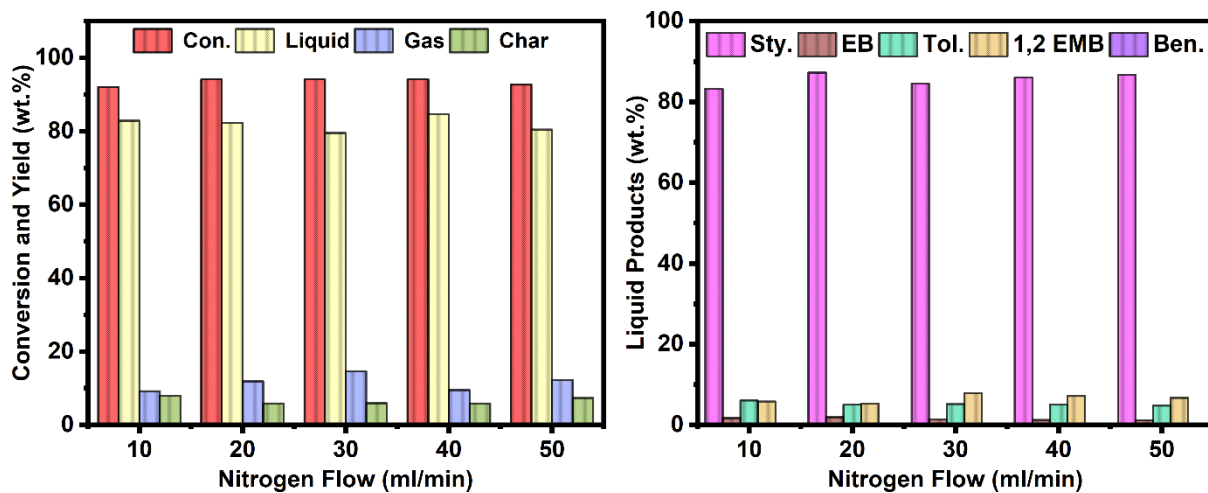
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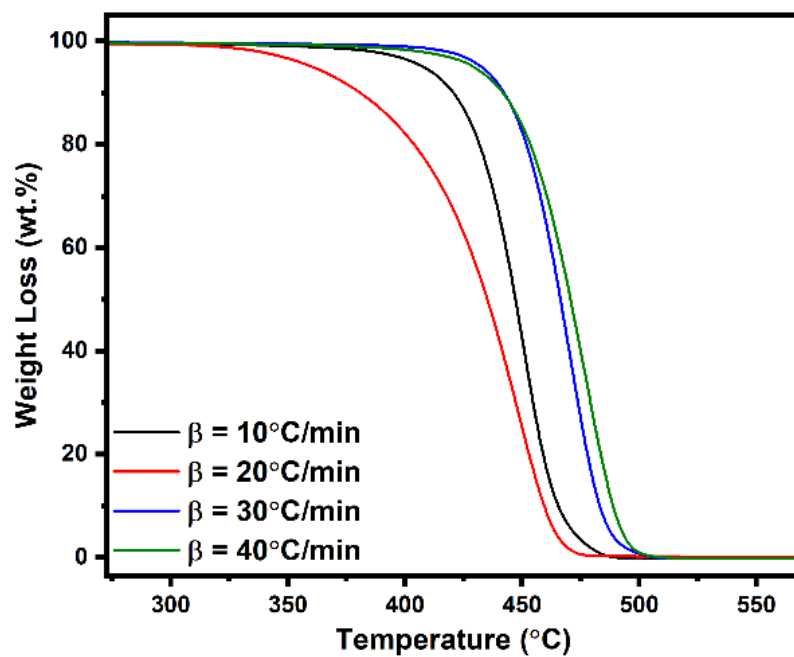
<sup>c</sup> Analytical Sciences Division, CSIR- Indian Institute of Petroleum, Haridwar Road, Dehradun, India 248005.



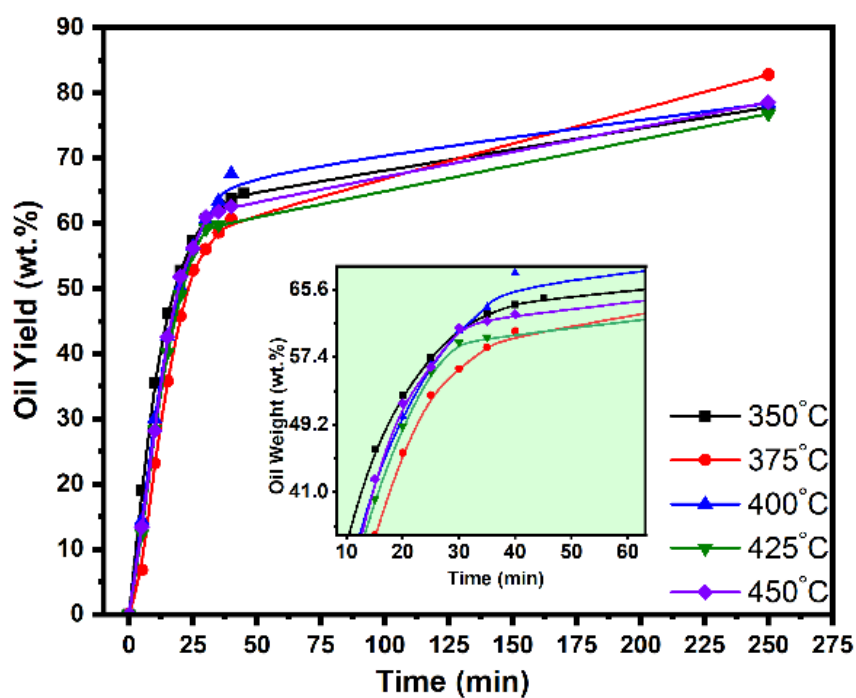
**Figure S1.** Depolymerization Reactor Setup



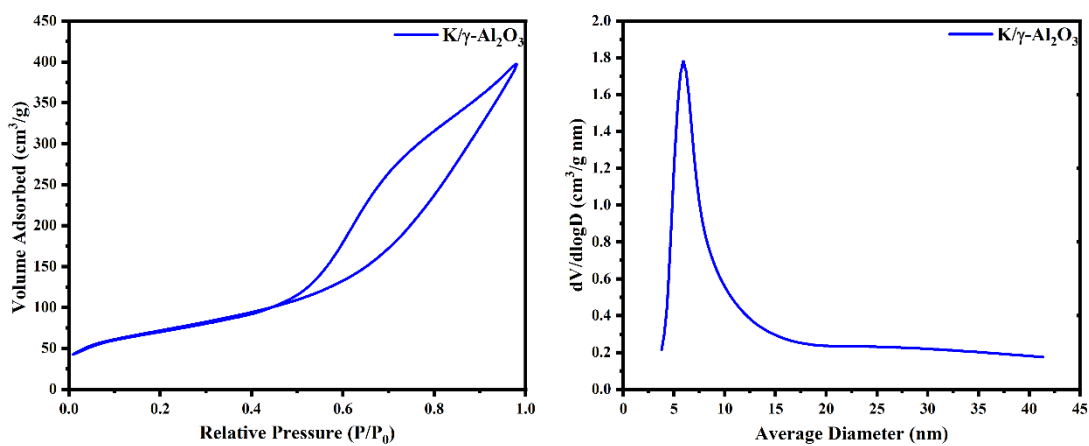
**Figure S2.** Effect of nitrogen flow rate (in terms of retention time) on product distribution over the 2%K-5%Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



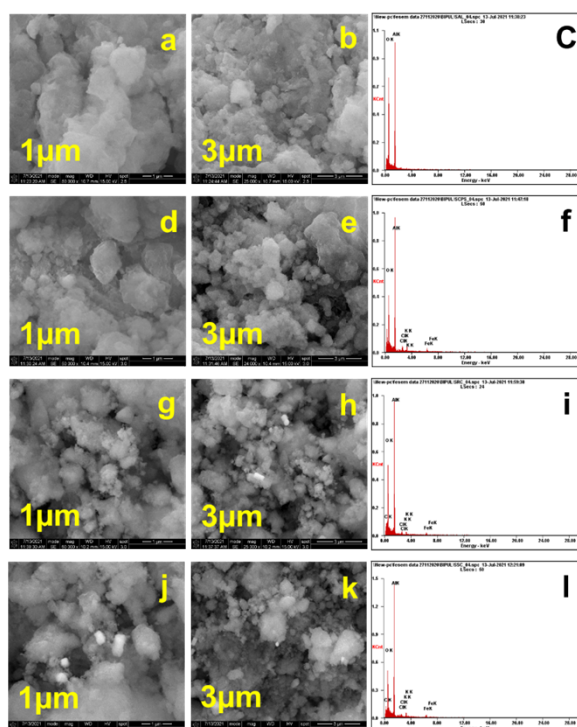
**Figure S3.** TGA of PS at a different ramping rate (10-40°C) under N<sub>2</sub> environment



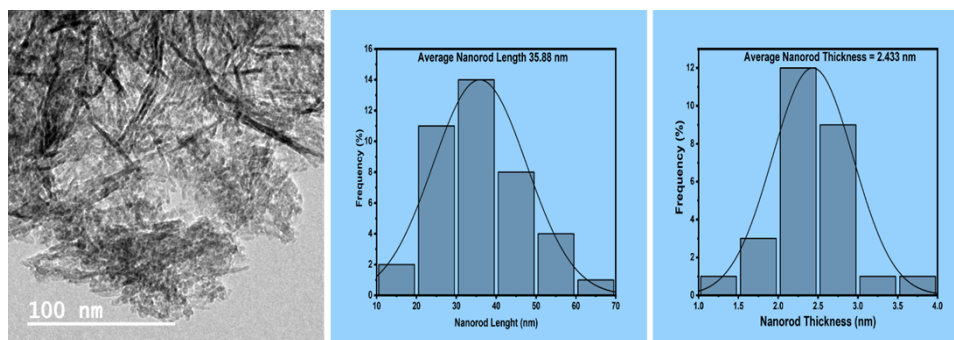
**Figure S4.** Catalytic degradation of PS on KFe/γ-Al<sub>2</sub>O<sub>3</sub> catalyst with variation in reactor temperature (350-450°C)



**Figure S5.** BET adsorption-desorption curve along with pore size distribution of K/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

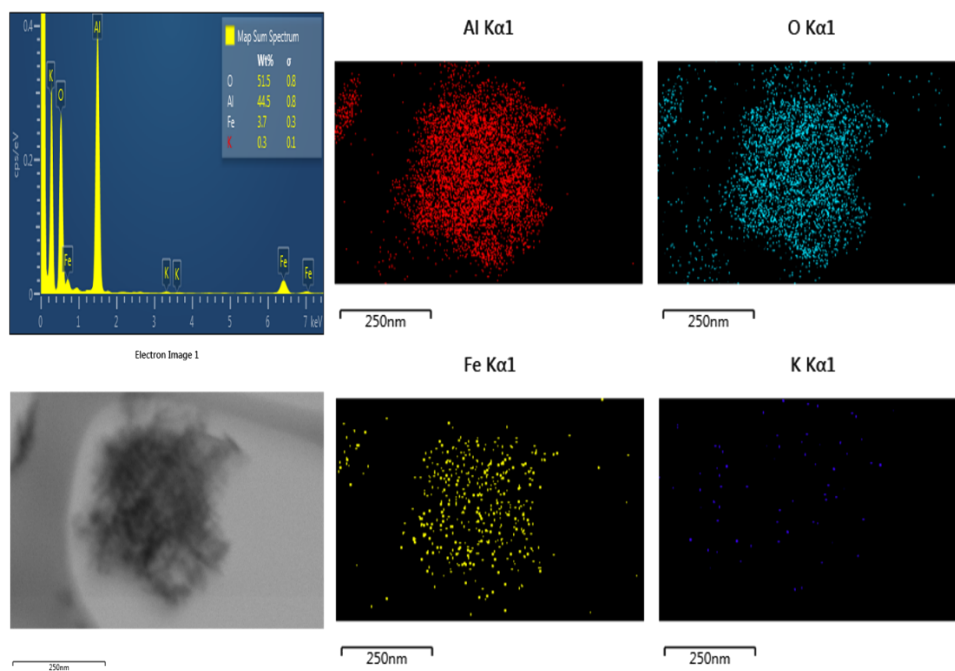


**Figure S6.** SEM images of PS depolymerization catalysts with corresponding EDX profile (a-c)  $\gamma$ - $\text{Al}_2\text{O}_3$ , (d-f)  $\text{KFe}/\gamma$ - $\text{Al}_2\text{O}_3$ , (g-i)  $\text{KFe}/\gamma$ - $\text{Al}_2\text{O}_3^{\text{Red}}$  and (j-l)  $\text{KFe}/\gamma$ - $\text{Al}_2\text{O}_3^{\text{Spent}}$

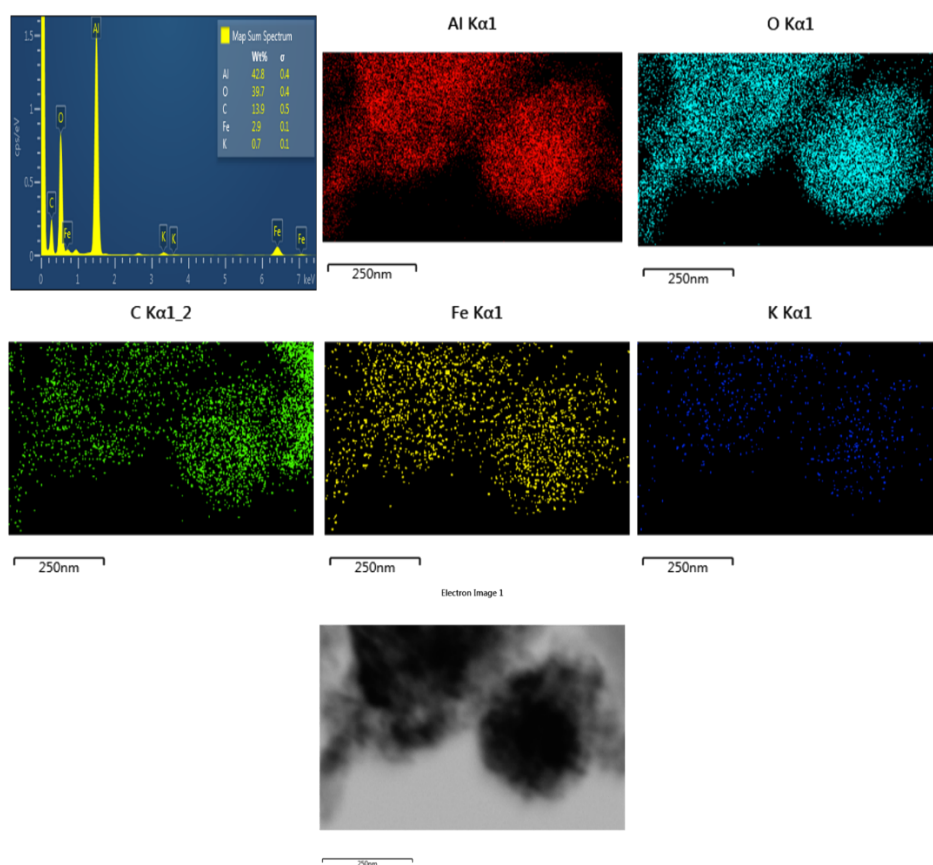


**Figure S7.** The dimension of the nanosized rod appears in the TEM analysis of catalyst ( $\text{KFe}/\gamma$ - $\text{Al}_2\text{O}_3$ )

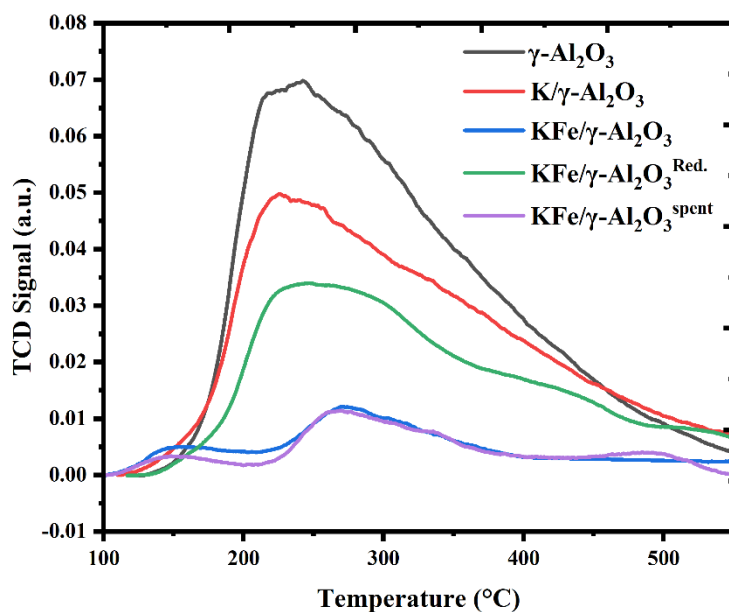
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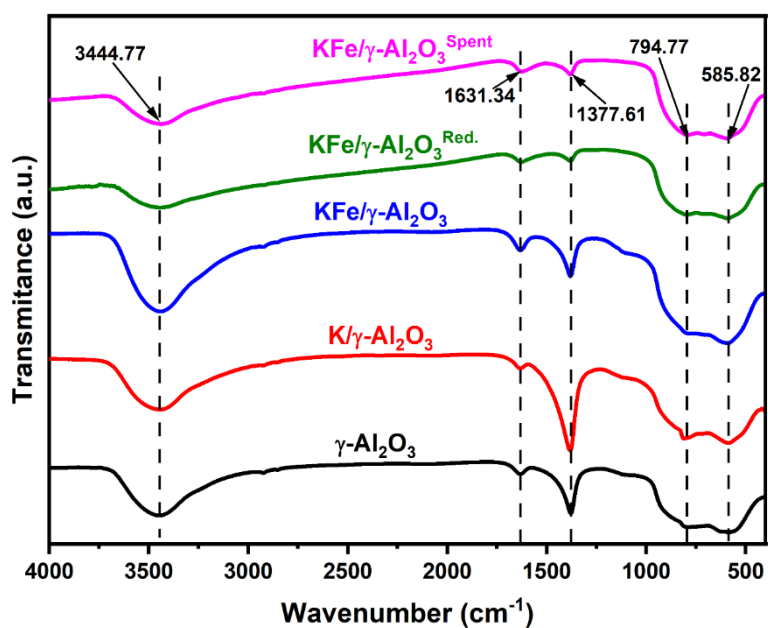
**Figure S8.** TEM EDX with elemental Mapping of catalyst (KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)



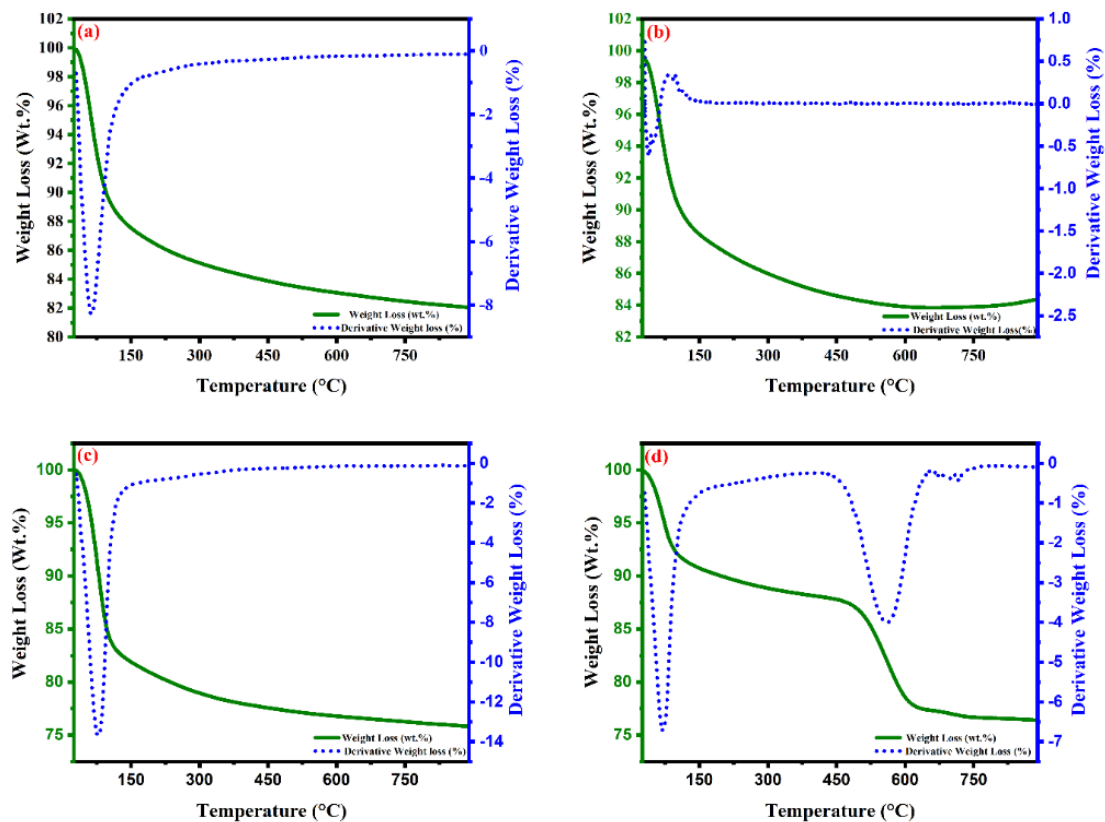
**Figure S9.** TEM EDX with elemental mapping of spent catalyst (KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>Spent</sup>)



**Figure S10.** NH<sub>3</sub>-TPD of different alumina catalysts. ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, K/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>Red.</sup>, and KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>Spent</sup>)



**Figure S11.** FT-IR spectroscopy of catalysts used in PS depolymerization



**Figure S12.** Thermogravimetric analysis of (a)  $\gamma\text{-Al}_2\text{O}_3$  (b)  $\text{K}/\gamma\text{-Al}_2\text{O}_3$  (c)  $\text{KFe}/\gamma\text{-Al}_2\text{O}_3$  (d)  $\text{KFe}/\gamma\text{-Al}_2\text{O}_3^{\text{Spent}}$

**Table S1.** Product distribution in depolymerisation PS

Catalyst	Liquid Yield (wt.%)	Gaseous yield (wt.%)	Residue Yield (wt.%)	Conversion (wt.%)
Thermal	71.2	6.7	22.0	78.0
$\gamma\text{-Al}_2\text{O}_3$	70.2	21.9	7.8	92.1
$\text{K}/\gamma\text{-Al}_2\text{O}_3$	75.1	11.3	13.5	86.5
$\text{K-Fe}/\gamma\text{-Al}_2\text{O}_3$	82.8	9.19	7.96	92.0

**Table S2.** The gaseous product distribution is shown below in the table with all the catalysts used in the PS depolymerization process.

S.No.	Catalyst	Hydrogen (mol.%)	Methane (mol.%)	Ethylene (mol.%)	Propylene (mol.%)	Other Hydrocarbons (mol.%)
1	Thermal	-	48.79	42.01	4.65	0.93
2	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	89.14	5.69	3.76	1.11	0.30
3	K/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	79.43	10.53	7.97	1.31	0.76
4	KFe/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	91.37	3.428	3.31	1.88	0.02

**Table S3.** Product distribution in the catalytic (KFe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) degradation of PS at different Temperatures shown in the table below

	Temperature (°C)				
	350	375	400	425	450
Y <sub>oil</sub>	77.78	82.84	78.55	76.86	78.54
Y <sub>char</sub>	3.51	7.97	3.94	3.87	3.51
Y <sub>gas</sub>	18.71	9.19	17.51	19.20	17.59
Product Composition					
Benzene	0.08	0.1	0.16	0.24	0.3
Toluene	6.21	6.07	6.33	6.55	7.15
Ethylbenzene	1.47	1.70	2.26	3.35	4.43
Styrene	86.69	83.202	84.905	82.955	81.639
1,2-ethyl methyl benzene	4.94	5.80	5.75	5.62	5.97
others	0.61	3.14	0.6	1.285	0.51

### Crystallite Size Calculation

Scherrer's Formula to Estimate average Crystallite size

Scherrer equation (also referred to as the Debye–Scherrer equation) has been applied to estimate the crystallite size measurement. The XRD curve (Shown in Figure 5a). It is used to resolve the size of crystals in the form of powder. The Scherrer equation can be written as:

$$t (\text{Å}) = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

Where,

$t$  = mean size of the crystalline domains (Å)

$K$  = dimensionless shape factor (0.9)



$\lambda$  = X-ray wavelength of  $\text{Cu}_\alpha$  (1.54 Å)

$\beta$  = FWHM (full width at half max) in Radian

$\theta$  = Bragg's angle This table involved the data extracted from the XRD spectrum of the catalyst (shown in Figure 5a)

**Example:**

Case of  $\gamma\text{-Al}_2\text{O}_3$  calcined at 550°C

For  $2\theta = 66.79^\circ$

$$\cos \theta = \cos \frac{66.79}{2} = 0.8349$$

FWHM ( $\beta$ ) = 2.75 degree (from XRD plot)

$$\beta = \frac{\pi \times \text{FWHM (in deg.)}}{180}$$

$$\beta = \frac{(3.14 \times 2.75)}{180}$$

$$\beta = 0.04797 \text{ (in radian)}$$

Therefore, the Crystallite Size of  $\gamma\text{-Al}_2\text{O}_3$  from equation (1) shown above

$$t = \frac{[0.9 \times 1.54]}{[0.04797 \times 0.8349]}$$

$$t = 34.61 \text{ \AA}$$

$$t = 3.46 \text{ nm}$$

The  $\gamma\text{-Al}_2\text{O}_3$  has the crystallite size of 3.46 nm (Calculated Above)

Similarly, we can apply this calculation to all the used catalysts and the crystallite size (Calculated by Scherrer's Equation) shown in the Table S4 given below:

**Table S4.** Calculated Crystallite size measurement of all the catalysts used in PS Depolymerization concerning the Alumina support

Catalyst	Bragg's Angle ( $\theta$ ) (degree)	$\text{Cos}\theta$	FWHM ( $\beta$ ) (radian)	Crystallite Size(t) (nm)
$\gamma\text{-Al}_2\text{O}_3$	33.40	0.8349	0.04797	3.46
K/ $\gamma\text{-Al}_2\text{O}_3$	33.42	0.8347	0.04117	4.03
KFe/ $\gamma\text{-Al}_2\text{O}_3$	33.37	0.8351	0.03960	4.19
KFe/ $\gamma\text{-Al}_2\text{O}_3^{\text{Red.}}$	33.32	0.8356	0.03541	4.68
KFe/ $\gamma\text{-Al}_2\text{O}_3^{\text{Spent}}$	33.37	0.8351	0.03314	5.01

### TGA-Thermal Pyrolysis Pathway

Kissinger's method for thermal degradation is also used in the kinetic data collected with the TG analyser. The kinetic parameters are calculated using Kissinger's method, which employs the temperature at which the rate of mass loss is maximum ( $T_m$ ), as illustrated by the equation (1):

$$\frac{E_a \beta}{RT_m^2} = An(1 - \alpha_m)^{(n-1)} e^{-\frac{E_a}{RT_m}} \quad (1)$$

where  $T_m$  and  $\alpha_m$  are the maximum degradation rate, temperature, and weight loss fraction, respectively, and  $\beta$  is the heating rate ( $\beta = dT/dt$ ). The degradation is considered to be first order, and conversion is independent of heating rate. For 1<sup>st</sup> order kinetics ( $n=1$ ), the equation (1) can be modified as equation (2):

$$\frac{E_a \beta}{RT_m^2} = A e^{-\frac{E_a}{RT_m}} \quad (2)$$

The TGA pattern at different heating rate is shown at Figure S3. The thermal activation energy of PS degradation is determined from the parameters of the straight line obtained

by plotting the dependence  $\ln(\beta/T_m^2)$  vs.  $1/T_m$

### Kinetics Experimental

For the study of polystyrene (PS) catalytic degradation in a parallel reactor configuration with a constant pyrolyzer and line heater temperature of 375°C and 130°C, respectively. On a reactor with a temperature range of 350 to 450°C, this experiment was carried out to determine the activation energy of the catalytic process. During PS depolymerisation, most of the solid feed (about 80%) turned to oil. Only the oil yield with time was measured in the catalytic activation energy calculation. Kinetic studies on the catalytic degradation were carried out using the experimental results from Figure S4.