

# Catalytic Activity of Aluminum Impregnated Catalysts for the Degradation of Waste Polystyrene

J. Shah, M. Rasul Jan, Adnan

**Abstract**—The aluminum impregnated catalysts of Al-alumina (Al-Al<sub>2</sub>O<sub>3</sub>), Al-montmorillonite (Al-Mmn) and Al-activated charcoal (Al-AC) of various percent loadings were prepared by wet impregnation method and characterized by SEM, XRD and N<sub>2</sub> adsorption/desorption (BET). The catalytic properties were investigated in the degradation of waste polystyrene (WPS). The results of catalytic degradation of Al metal, 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC were compared with each other for optimum conditions. Among the catalyst used 20% Al-Al<sub>2</sub>O<sub>3</sub> was found the most effective catalyst. The BET surface area of 20% Al-Al<sub>2</sub>O<sub>3</sub> determined was 70.2 m<sup>2</sup>/g. The SEM data revealed the catalyst with porous structure throughout the frame work with small nanosized crystallites. The yield of liquid products with 20% Al-Al<sub>2</sub>O<sub>3</sub> (91.53 ± 2.27 wt%) was the same as compared to Al metal (91.20 ± 0.35 wt%) but the selectivity of hydrocarbons and yield of styrene monomer (56.32 wt%) was higher with 20% Al-Al<sub>2</sub>O<sub>3</sub> catalyst.

**Keywords**—Impregnation, catalytic degradation, waste polystyrene, styrene.

## I. INTRODUCTION

POLYSTYRENE (PS) has wide range of uses. It is fourth large consuming plastic in the world [1], [2]. PS is used in drinking cups, toys, molded parts inside of cars, and the household articles like computers, hairdryers, and kitchen appliances. It is widely used as shock resistant material in packing for the transport of fragile and delicate goods and as insulating materials in buildings and refrigerator industry etc. [1], [3]. Demand of PS has increased due to its unique desirable properties and also due to the rapid growth of population and industry causing huge quantity refusal of solid waste [1], [4]. Among the total municipal solid waste PS is only 9% and it is not recycled [5].

An alternate and best option for the disposal of PS is converting them into useful oil and gases or other important products to reduce its impact on the environment [6]-[8]. Degradation has a key role in polymer recycling, to either convert them into fuel oils, or its monomers by thermal degradation. Styrene monomer can be recovered with thermal degradation of PS but with poor yield [9]. The selection and development of suitable catalysts, not only enhances the yield of styrene monomer but also lowers the degradation temperature and time resulting reduce production costs [9]-[11].

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Recent trends in PS degradation are the use of modified, promoted or impregnated catalysts. In the literature only few researchers have performed work on impregnated or modified catalysts for the degradation of PS. Tae et al. [12] worked on acid-treated halloysite clays and found that with increase of contact time and catalyst acidity results in increased ethylbenzene while higher temperature favored the production of styrene monomer. Xie et al. [9] used base modified silicon mesoporous molecular sieve (K<sub>2</sub>O/Si-MCM-41) and found it with better catalytic activity. Kim et al. [13] investigated modified alumina support with Fe, K, Ba, Zn and Mg for PS degradation and found Fe-K/Al<sub>2</sub>O<sub>3</sub> best catalyst with significant production of liquid.

Unfortunately, these catalysts produce small amount of products with relatively low selectivity. The aim of the present work was to prepare an impregnated catalyst to improve the catalytic activity. In the reported work aluminum (Al) impregnated on alumina (Al<sub>2</sub>O<sub>3</sub>), montmorillonite (Mmn) and activated charcoal (AC) as base materials were prepared and used for catalytic degradation of PS.

## II. EXPERIMENTAL

### A. Materials and Methods

Waste polystyrene (WPS) granules with 0.1-0.78 mm in size (20 times reduced size of expanded PS), each bead with an average molecular weight Mw = 200,000 g/mol. Aluminum powder (90%) and alumina (1-5 mm particle size) was purchased from E. Merck, Darmstadt, Germany, AlCl<sub>3</sub>. 6H<sub>2</sub>O was supplied by BDH Laboratory Supplies, Poole, BH151TD, England, activated charcoal powder was supplied by Haq Chemicals Pakistan and montmorillonite was received from local contractor. For the degradation experiments a Pyrex glass reactor was used, the samples of WPS were degraded in the presence of appropriate amount of catalyst. The yield of liquids, gases and residue left were measured after degradation experiments and are expressed in terms of wt.% of WPS degraded.

### B. Catalyst Preparation

The Al impregnated catalyst was prepared using the incipient wetness method to give final catalyst composition of 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.% and 25 wt.% of Al over Al<sub>2</sub>O<sub>3</sub>, Mmn and AC supports. For impregnated catalysts preparation, 5.0 g of each support was mixed in appropriate amount of distilled water to make slurry. For each support 2.235 g, 4.47 g, 6.705 g, 8.94 g and 11.175 g of AlCl<sub>3</sub>. 6H<sub>2</sub>O were also dissolved in appropriate amount of distilled water and deposited on each support. The mixture was stirred for 1

hour at 60 °C. The catalyst was dried in oven at 120°C for 6 hours followed by calcination at 300°C for 4 hours. The aluminum supported catalysts were termed as Al-Al<sub>2</sub>O<sub>3</sub>, Al-Mmn and Al-AC with the preposition of percentage of the precursor metal are mentioned in (Table I).

TABLE I  
CATALYSTS COMPOSITION AND CODES

Precursor metal (Al) loading (wt.%)	Code of Catalyst using different supports		
	Al <sub>2</sub> O <sub>3</sub>	Mmn	AC
5	5% Al-Al <sub>2</sub> O <sub>3</sub>	5% Al-Mmn	5% Al-AC
10	10% Al-Al <sub>2</sub> O <sub>3</sub>	10% Al-Mmn	10% Al-AC
15	15% Al-Al <sub>2</sub> O <sub>3</sub>	15% Al-Mmn	15% Al-AC
20	20% Al-Al <sub>2</sub> O <sub>3</sub>	20% Al-Mmn	20% Al-AC
25	25% Al-Al <sub>2</sub> O <sub>3</sub>	25% Al-Mmn	25% Al-AC

### C. Catalyst Characterization

The surface area, pore volume and pore size were analyzed by Surface Area Analyzer NOVA2200e Quantachrome, USA for supports as well as impregnated catalysts. The analyses were carried out using liquid N<sub>2</sub> at 77.4 K with pre-degassing for 2 h at 100°C.

Scanning electron microscopy (SEM) images were obtained with 30 KV scanning electron microscope (JSM5910, JEOL, Japan).

The X-ray diffraction (XRD) patterns for each support and catalyst were recorded using JDX-3532 JEOL (Japan) diffractometer equipped with anode of Cu-K $\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ) at 40 KV and 30 mA in the 2 $\theta$  range of 10-80°.

Liquid fractions obtained from catalytic degradation of WPS were analyzed by GC/MS (Shimadzu QP2010 Plus). The instrument was configured with 95% dimethylpolysiloxane and 5% polyphenyl stationary phase and with a 30 m  $\times$  0.25 mm ID, 0.25  $\mu\text{m}$  film thickness DB-5MS (from J&W Scientific) fused silica capillary column. Helium was used with a flow rate of 1.5 mL/min as a carrier gas. The injector temperature was 300°C. The initial oven temperature was 35°C, held for 5 min. this temperature was ramped to 100°C at 5°C/min and held for 1 min. Then the temperature was raised to 150°C at 10°C/min, held for 10 min and finally the temperature was ramped to 290°C at 2.5°C/min and held for 10 min. The ion source temperature used was 280°C with interface temperature 290°C. Spectral library was used for ion mass spectra interpretation.

### D. Catalytic Activity

Catalytic degradation experiments were carried out in a Pyrex glass batch reactor, 7 cm internal diameter and 22 cm height provided with an external heating assembly operates up to 1000°C. WPS sample in mixture with corresponding amount of catalyst was loaded into the reactor, a solid-solid blend without the use of any solvent and heated with a rate of 25°C/min. All the experiments were carried out using triplicate analysis, the results of the experiments are consistent and within the statistical acceptable range. The degradation of WPS gave off liquids, gases and residues - the carbonaceous compounds stuck to the reactor wall.

Material balance calculations were performed using the following formula:

$$\% \text{ Conversion of Liquid} = \frac{\text{Wt of Liquid obtained}}{\text{Wt of WPS}} \times 100$$

$$\% \text{ Conversion of Gas} = \frac{\text{Wt of WPS} - (\text{Wt of Liquid} + \text{Wt of Residue})}{\text{Wt of WPS}} \times 100$$

$$\text{Total \% Conversion} = \frac{(\text{Wt of WPS} - \text{Wt of Residue})}{\text{Wt of WPS}} \times 100$$

## III. RESULTS AND DISCUSSIONS

### A. Catalyst Characterization

Surface properties like surface area, pore size and pore volume of all catalysts and the supports used for their preparation were determined (Table II). The BET surface area of 20% Al-Al<sub>2</sub>O<sub>3</sub> and 5% Al-Mmn changed slightly in comparison with their supports while it decreased greatly in case of 20% Al-AC catalyst).

TABLE II  
SURFACE AREA, PORE VOLUME AND PORE SIZE DATA FOR AL IMPREGNATED CATALYSTS STUDIED

Parameter	Catalysts					
	Al <sub>2</sub> O <sub>3</sub>	20% Al-Al <sub>2</sub> O <sub>3</sub>	Mmn	5% Al-Mmn	AC	20% Al-AC
Surface Area ( m <sup>2</sup> /g)	68.3	70.2	116	102.2	335	66.3
Pore Volume (m <sup>3</sup> /g)	0.38	0.10	1.25	1.23	0.11	0.06
Pore Size (Å)	120	79.3	116	118.96	23.3	34.5

The surface morphology of impregnated catalysts and support were determined with SEM. Fig. 1 (a) gives information about the surface of Al<sub>2</sub>O<sub>3</sub> support having oval discs like particles with 2-3  $\mu\text{m}$  in size. SEM micrograph of Fig. 1 (b) corresponds to surface information about 20% Al-Al<sub>2</sub>O<sub>3</sub> catalyst. The SEM photograph exhibit rough surface structure with major and minor cracks throughout the catalyst surface, which is due to the overlapping and accumulation of nano-crystalline structures having crystal size about 300-500nm. Mmn support is shown in Fig. 2 (a) which depicts 10-30  $\mu\text{m}$  uniform and porous particles where it's Al impregnated catalyst of 5% Al-Mmn presents peanut shape particles with 1-4  $\mu\text{m}$  particle size Fig. 2 (b). The edge brightness of each particle suggests the successful impregnation of Al metal over Mmn support. SEM of AC support indicates rough and porous surface (Fig. 3 (a)) and 20% Al-AC catalysts is shown in Fig. 3 (b) which also confirms the impregnation of precursor metal, the particle are in the form of large blocks having smooth surface area with particle size ranging from 0.5-30  $\mu\text{m}$ .

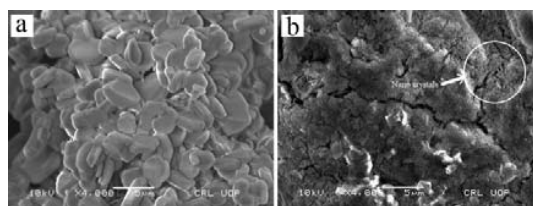


Fig. 1 SEM micrograph of (a) Al<sub>2</sub>O<sub>3</sub> support and (b) 20% Al-Al<sub>2</sub>O<sub>3</sub>

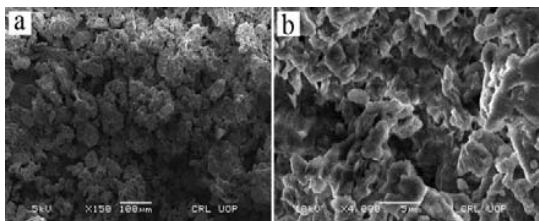


Fig. 2 SEM micrograph of (a) Mmn support and (b) 5% Al-Mmn

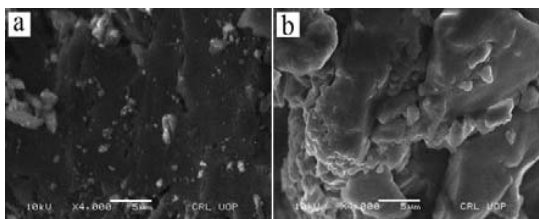


Fig. 3 SEM micrograph of (a) AC support and (b) 20% Al-AC

The XRD analysis of all the three bases and its impregnated catalyst were taken. The XRD patterns for  $\text{Al}_2\text{O}_3$  and impregnated catalyst of Al are given in Fig. 4 (a). The diffractogram shows the properties of pure  $\text{Al}_2\text{O}_3$  with major peaks at  $25.5^\circ$ ,  $35.2^\circ$ ,  $37.8^\circ$ ,  $43.5^\circ$ ,  $52.2^\circ$ ,  $61.4^\circ$ ,  $66.7^\circ$ ,  $76.9^\circ$  and  $77.2^\circ$  of  $2\theta$  with reference to ICDD Card No. 46212 and 520803. The XRD patterns of 20% Al- $\text{Al}_2\text{O}_3$  catalyst are shown in Fig. 4 (b). The patterns show major peaks of chloraluminite ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) according to ICDD Card No. 441473 at  $15.07^\circ$ ,  $27.19^\circ$ ,  $27.52^\circ$ ,  $35.05^\circ$ ,  $39.01^\circ$ ,  $41.38^\circ$ ,  $43.33^\circ$ ,  $51.94^\circ$  and  $68.35^\circ$  with rhombohedral geometry (JCPDS Card No. 44-1473) along with the peaks of aluminum chloride hydroxide hydrate ( $\text{Al}_{10}\text{Cl}_3(\text{OH})_{27} \cdot 13\text{H}_2\text{O}$ ) at  $27.19^\circ$ ,  $39.01^\circ$ ,  $52.63^\circ$  and  $57.67^\circ$  (ICDD Card No. 270009) having monoclinic system in accordance to JCPDS Card No. 27-0009. The XRD patterns for Mmn and 5% Al-Mmn catalysts are shown in Fig. 5 (a), the diffractograms for Mmn support at  $19.51^\circ$ ,  $25.24^\circ$ ,  $26.29^\circ$ ,  $29.41^\circ$ ,  $47.38^\circ$  and  $57.07^\circ$  indicates bredigite ( $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$ ) according to ICDD Card No. 360399, the patterns at  $20.62^\circ$ ,  $25.24^\circ$  and  $57.07^\circ$  also shows sodium magnesium silicate ( $\text{Na}_2\text{MgSiO}_4$ ) (ICDD Card No. 471499). Both the minerals have orthorhombic structures according to JCPDS Card No. 36-0399 and 47-1499, respectively along with peaks at  $19.51^\circ$ ,  $23.77^\circ$  and  $29.41^\circ$  shows montmorillonite-15A ( $\text{CaO}_2(\text{Al,Mg})\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) (ICDD Card No. 130135) having hexagonal geometry (JCPDS Card No. 13-0135). The XRD patterns for 5% Al-Mmn catalyst are shown in Fig. 5 (b), it shows the major peaks for silicon oxide ( $\text{Si}_3\text{O}_6$ ) at  $26.65^\circ$ ,  $27.64^\circ$ ,  $35.17^\circ$  and  $45.40^\circ$  (ICDD Card No. 520144) that is in hexagonal system according to JCPDS Card No. 52-0144. The patterns also shows at  $31.75^\circ$  and  $62.02^\circ$  sodium aluminum silicate ( $\text{Na}_{1.15}\text{Al}_{1.15}\text{Si}_{0.85}\text{O}_4$  and  $\text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4$ ) according to ICDD Card Nos. 490007 and 490004, respectively both with orthorhombic geometry. The catalyst also consist a small amount of magnesium aluminum oxide ( $\text{MgAl}_2\text{O}_3$ ) and magnesium aluminum silicate ( $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ ) residue

according to ICDD Card No. 211152 and 150742. AC support is indicated at  $26.59^\circ$  in Fig. 6 (a) according to ICDD Card No. 261076 with hexagonal system structure with JCPDS Card No. 26-1076. The Fig. 6 (b) shows 20% Al-AC and consist diffractogram maximum major peaks for monoclinic (JCPDS Card No. 22-0010) aluminum chloride ( $\text{AlCl}_3$ ) at  $17.26^\circ$ ,  $26.62^\circ$ ,  $30.31^\circ$ ,  $36.55^\circ$ ,  $62.59^\circ$ ,  $66.34^\circ$ ,  $73.57^\circ$  and rhombohedral (JCPDS Card No. 50-1086) carbon (charcoal) at  $44.17^\circ$ ,  $46.69^\circ$  and  $70.96^\circ$  according to ICDD Card Nos. 220010 and 501086, respectively. The catalyst XRD patterns also show hexachloromethane ( $\text{C}_2\text{Cl}_6$ ) at  $17.26^\circ$ ,  $30.31^\circ$ ,  $36.55^\circ$ ,  $38.98^\circ$ ,  $46.69^\circ$ ,  $49.36^\circ$  and dienochlor ( $\text{C}_{10}\text{Cl}_{10}$ ) at  $11.29^\circ$ ,  $13.78^\circ$  and  $27.52^\circ$  according to ICDD Card Nos. 110841 and 411905 with orthorhombic and monoclinic geometry, respectively.

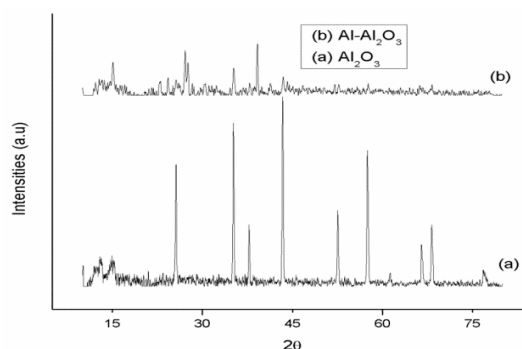
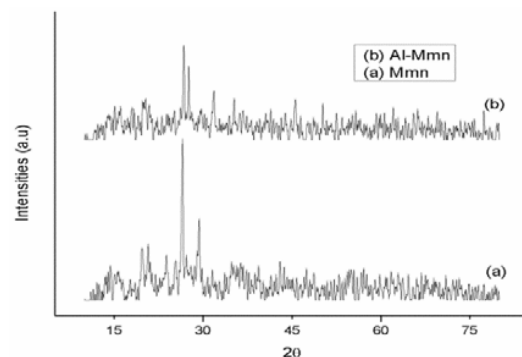
Fig. 4 XRD diffractogram of  $\text{Al}_2\text{O}_3$  support versus 20% Al- $\text{Al}_2\text{O}_3$  catalyst

Fig. 5 XRD diffractogram of support Mmn support versus 5% Al-Mmn catalyst

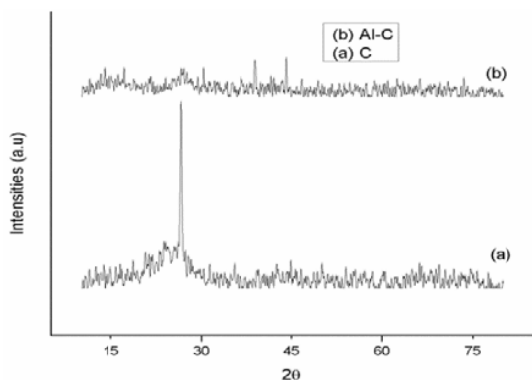


Fig. 6 XRD diffractogram of charcoal support versus 20% Al-AC catalyst

### B. Catalyst Activity

The catalytic activity of three catalysts systems prepared determined for the degradation of WPS. The activity of catalysts were tested with the effect of various parameters like temperature, time and polymer to catalyst ratio for maximum amount of liquid and selection of the degraded products of WPS.

#### 1. Effect of Temperature

Using Al metal catalyst (polymer to catalyst ratio 1:0.2 and 60 min heating time) the temperature effect was checked for the degradation of WPS from 250 °C to 500 °C range (Fig. 7). The yield of liquid products at 400 °C was  $56.13 \pm 7.51$  wt.% and increased with increase of temperature from 250 °C to 500 °C. The yield of liquid products were maximum i.e.  $91.53 \pm 2.27$ wt.% at 500 °C with 100% total conversion.

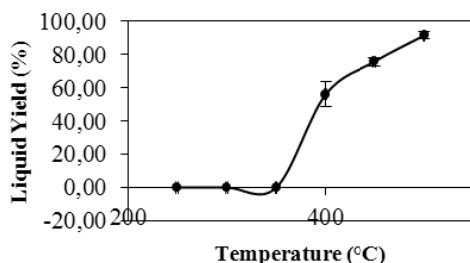


Fig. 7 Effect of temperature using Al catalyst (Reaction conditions; time 60 min, polymer to catalyst ratio 1:0.2)

#### 2. Effect of Time

The degradation of WPS was optimized for the effect of heating time (polymer to catalyst ratio 1:0.2 and heating temperature 500°C) from 30 to 150 min (Fig. 8). The liquid products were increased with increase of heating time from 30 min to 60 min and no change was observed when the heating time was increased beyond 60 min. The amount of liquid yield remained almost constant with further increase in heating time. Thus 60 min was considered optimum time for the degradation of WPS with  $91.53 \pm 2.27$  wt.% of liquid yield with 100% total conversion.

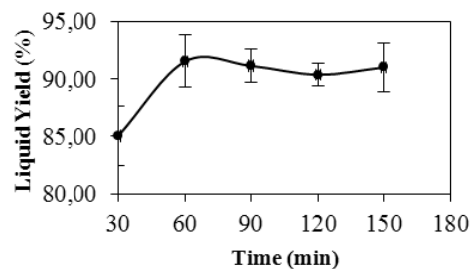


Fig. 8 Effect of time using Al catalyst (Reaction conditions; temperature 500 °C, polymer to catalyst ratio 1:0.2)

#### 3. Effect of Polymer to Catalyst Ratio

WPS degradation was carried out using Al metal (Al) as catalyst (Fig. 9) and its impregnated catalysts (20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC) shown in Fig. 10. Initially the WPS were degraded at optimized temperature and time using Al metal as catalyst. It was used in the polymer to catalyst ratio of 1:0.1 to 1:0.5. The amount of liquid product increased with a small fraction when the polymer to catalyst ratio was changed from 1:0.1 to 1:0.2 and with further increase in polymer to catalyst ratio, it causes no significant change in the amount of liquid products. The maximum percent yield of liquid products were obtained with 1:0.2 polymer to catalyst ratio i.e.  $91.53 \pm 2.27$  wt.%.

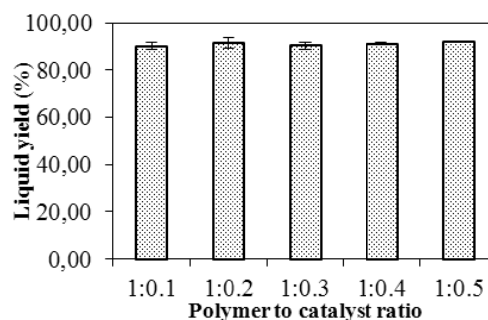


Fig. 9 Effect of polymer to catalyst ratio using Al catalysts (Reaction conditions; temperature 500 °C, time 60 min)

The effect of percentage of the precursor metal (Al) was also checked for the three systems of catalysts using three types of supports (Table I). The precursor metal percentage was optimized using optimum temperature, time and polymer to catalysts ratio of Al metal catalyst. 5% to 25% catalysts of Al-Al<sub>2</sub>O<sub>3</sub>, Al-Mmn and Al-AC were applied for the degradation of WPS (Fig. 10). In case of Al-Al<sub>2</sub>O<sub>3</sub> and Al-AC catalyst the yield of liquid products increased with increase of percentage of precursor metal (Al) up to 20% and increased to a maximum and with further increase no significant change was observed, the yield of liquid products with 20% Al-Al<sub>2</sub>O<sub>3</sub> was  $91.20 \pm 0.35$  wt.% and with 20% Al-AC was  $88.87 \pm 0.81$ %. While with Al-Mmn catalyst, the yield of liquid products was  $89.60 \pm 0.20$  wt.% maximum with 5% Al-Mmn and remained constant with increase of Al percentage. The maximum yield of liquid products was with 20% Al-Al<sub>2</sub>O<sub>3</sub>,

5% Al-Mmn and 20% Al-AC catalysts i.e.  $91.20 \pm 0.35$  wt.%,  $89.60 \pm 0.20$  wt.% and  $88.87 \pm 0.81$  wt.% with 100%, 92% and 100% total conversion, respectively.

The degradation of WPS was also carried out with supports used for the impregnation of Al and the results of investigation are reported in Table III. The yield of liquid products was almost the same, 91 wt.% as those of Al metal, 20% Al-Al<sub>2</sub>O<sub>3</sub> and 5% Mmn catalysts, however, the quality of liquid products yield is important and the selectivity of products is considered as measure of the quality of liquid products formed.

### C. Composition of Liquid Products

The maximum liquid products obtained with Al metal, 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC were subjected for GC-MS analysis. The yield of compounds was expressed in terms of wt.% of WPS employed.

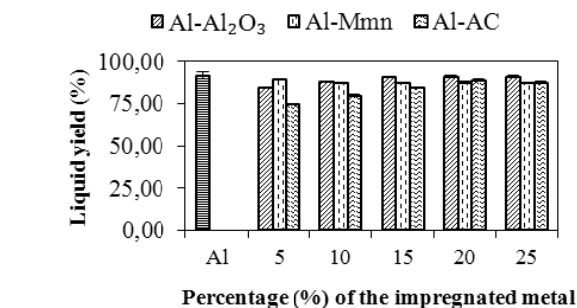


Fig. 10 Effect of impregnated Al percentage over supports (Al<sub>2</sub>O<sub>3</sub>, Mmn and AC) for maximum liquid production (Reaction conditions: Temperature 500 °C, time 60 min and polymer to catalyst ratio 1:0.2)

TABLE III  
COMPARISON OF REACTION CONDITION AND YIELD OF PRODUCTS USING THERMAL DEGRADATION SUPPORTS AND ALUMINUM IMPREGNATED CATALYST

	Al	Al <sub>2</sub> O <sub>3</sub>	20% Al-Al <sub>2</sub> O <sub>3</sub>	Mmn	5% Al-Mmn	AC	20% Al-AC
<i>Reaction conditions</i>							
Temperature (°C)	500	450	500	450	500	500	500
Time (min.)	60	60	60	60	60	30	60
Pol. to Cat. ratio	1:0.2	1:0.2	1:0.2	1:0.2	1:0.2	1:0.1	1:0.2
<i>Content of products (wt.%)</i>							
Liquid yield	91.5	87.0	91.2	91.3	89.6	84.5	88.9
Gas yield	8.5	13.0	8.7	8.7	2.4	15.5	10.7
Residue					8.0		
Total Conversion	100.0	100.0	100.0	100.0	92.0	100.0	100.0

The results of analysis are tabulated in Table IV for Al, 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC catalysts. The maximum yield of high molecular weight aromatic hydrocarbons was with Al metal catalyst with least number of products while the maximum yield of lower molecular weight aromatic hydrocarbons was with impregnated catalysts. Toluene, ethylbenzene, styrene, alpha-methylstyrene, benzene, 1,1(1,1,2,2-tetramethyl-1,2-ethanediyl) bis, benzene, 3-butynyl and 1,2-propanediol, 3-benzyloxy-1,2-diacetyl were the major and prominent compounds with almost all the catalysts. Benzene was not formed with Al metal as catalyst while the yield of benzene was negligible using Al impregnated catalysts i.e., 1.13%, 0.81% and 1.42% with 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC, respectively. The yield of toluene was highest with 20% Al-Al<sub>2</sub>O<sub>3</sub> (9.47%) and minimum with Al metal as catalyst. Ethylbenzene was 8.90% maximum with 20% Al-AC. Styrene monomer was the major component of the degradation products; it was 47.89%, 56.52%, 49.28% and 47.29% with Al metal, Al-Al<sub>2</sub>O<sub>3</sub>, Al-Mmn and Al-AC catalysts, respectively. Styrene monomer was maximum (56.52%) with 20% Al-Al<sub>2</sub>O<sub>3</sub>. Benzene, 3-butynyl (14.64%) and 1,2-propanediol, 3-benzyloxy-1,2-diacetyl (14.57%) were the second major compounds with Al catalyst and the yield of other compounds were in smaller amount using Al impregnated catalysts. Like benzene, 3-butynyl was 0%, 5.58% and 4.94%, 1,2-propanediol, 3-benzyloxy-1,2-diacetyl was 0%, 0% and 1.55% with 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC catalysts, respectively.

The percent composition of alpha-methylstyrene was 1.32%, 1.72%, 2.80% and 1.38% and the percent composition of benzene, 1,1, (1,2-ethanediyl) bis was 1.44%, 0%, 3.56% and 1.35% with Al, 20% Al-Al<sub>2</sub>O<sub>3</sub>, 5% Al-Mmn and 20% Al-AC catalysts, respectively. Beside these, other compounds in a smaller concentration were formed with the degradation of WPS using Al metal and its impregnated catalysts.

The results of the previous reported methods were compared with 20% Al-Al<sub>2</sub>O<sub>3</sub>, given in Table V. According to the findings the yield of benzene and toluene was higher with 20% Al-Al<sub>2</sub>O<sub>3</sub> than the reported catalysts, where the yield of styrene monomer was approximately the same with 9% K<sub>2</sub>O/Si-MCM-41 it was less than that of Fe-K/Al<sub>2</sub>O<sub>3</sub> and so for alpha methylstyrene. The yield of low molecular weight aromatic hydrocarbons was greater using 20% Al-Al<sub>2</sub>O<sub>3</sub> as compared to the reported catalysts in the literature. The percentages of other hydrocarbons were also higher in the reported methods.

### IV. CONCLUSION

Al and its impregnated catalysts using Al<sub>2</sub>O<sub>3</sub>, Mmn and AC as supports were prepared. The active catalysts were characterized using surface area, SEM and XRD. The results of liquid products yield and GC-MS characterization revealed that 20% Al-Al<sub>2</sub>O<sub>3</sub> with good catalytic activity producing  $91.20 \pm 0.35$  wt.% liquid products with low molecular weight hydrocarbons. The amount of light weight aromatic was high

as compared to other catalysts used with major fraction of styrene monomer i.e. 56.52%.

TABLE IV  
COMPARISON OF PRODUCTS FORMED BY PS DEGRADATION USING THERMAL DEGRADATION, AL METAL CATALYST, AL IMPREGNATED CATALYST AND SUPPORTS USED AS CATALYSTS

Products	Al	Al <sub>2</sub> O <sub>3</sub>	20% Al-Al <sub>2</sub> O <sub>3</sub>	Mmn	5% Al-Mmn	AC	20% Al-AC
Benzene	0.0	0.00	1.13	0.04	0.81	0.32	1.42
Toluene	3.2	2.58	9.47	1.57	8.49	6.96	8.49
3-Hexen-2-one			6.10				
2-Pentanone, 4-hydroxy-4-methyl-			0.96		0.88	0.25	0.34
Ethylbenzene	1.5	1.40	5.6	0.49	5.13	6.55	8.90
2-Hexene-2-one			5.1				
Styrene	47.9	45.65	56.3	44.89	49.28	43.61	47.29
Benzene, (1-methylethyl)-	0.04	0.03	0.3	0.01	0.28	0.47	0.76
alpha.-methylstyrene	1.3	1.11	1.7	0.69	2.80	2.62	1.38
Indene			0.7				
alpha.-Chloro-xylene			0.7	0.01		0.03	1.86
Benzene, 1,1'-(1,1,2,2-tetramethyl-1,2-ethanediyl)bis			1.9	0.01	0.20	0.05	1.27
Naphthalene	0.12	0.04	0.7	0.01	0.62	0.44	0.44
3-Ethyl-3-methylheptane	0.01	0.02			0.50	0.11	0.04
Benzene, 1,1'-(1,2-ethanediyl)bis	1.44	0.94		0.74	3.56	4.29	1.35
Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis	0.54	0.47		0.31	1.69	1.89	0.97
Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)	0.05	0.05		0.06		0.67	
Benzene, 1,1'-(1,3-propanediyl)bis	0.70	0.98		0.81	0.41		0.48
Phenanthrene	0.16	0.09		0.07	0.52	0.53	0.25
Benzene, 3-butynyl	14.6	14.29		18.14	5.58	6.87	4.94
Benzene, (1-methyl-3-butenyl)	0.64	0.72		0.71	0.55	0.64	0.44
Anthracene					0.60	0.57	0.30
Benzene, (1-ethyl-2-propenyl)	0.40	0.39		0.50	0.09	0.11	0.17
2-Phenylnaphthalene	0.50	0.45		0.10	1.84	1.57	1.77
p-Terphenyl	0.13	0.08		0.04	0.53	0.47	0.24
1,2-propanediol, 3-benzyloxy-1,2-diacetyl	14.6	13.75		18.79		0.52	1.55
1,1':3,1''-Terphenyl, 5'-phenyl	0.27	0.36		0.29	0.41	0.67	0.36
Other Hydrocarbons	3.41	3.61	0.6	3.05	4.84	4.26	4.28
Gases + Residue	8.47	13.00	8.7	8.67	10.40	15.53	10.70

TABLE V  
COMPARISON OF REACTION CONDITIONS, THEIR CONTENTS AND LIQUID PRODUCTS FORMED DURING THE DEGRADATION OF PS IN REPORTED LITERATURE (BY WT.% OF THE OIL/FORMULA APPLIED) WITH 20% AL-AL<sub>2</sub>O<sub>3</sub>

	Current Method	Literature Method				
	20% Al-Al <sub>2</sub> O <sub>3</sub>	9% K <sub>2</sub> O/Si-MCM-41[9]	HY-700 [14]	HH [12]	HDM (147) [15]	Fe-K/Al <sub>2</sub> O <sub>3</sub> [8]
<i>Reaction conditions</i>						
Temperature	500	400	375	450	360	400
Time	60	30	90	120	90	90
Pol. to Cat. ratio	1:0.2	2:1	1:0.01	-	1:0.01	1:0.01
<i>Content of products (wt.%)</i>						
Yield Oil	91.53	85.7	68.0	90.2	59.00	92.2
Yield Gas	8.47	4.9	18.8	4.8	22.70	6.4
Residue	0.00	9.5	13.2	5.0	18.30	1.4
<i>Contents of oils (wt.%)</i>						
Benzene	1.13	-	0.20	0.23	0.04	0.09
Toluene	9.47	-	4.9	6.44	3.37	5.7
Ethylbenzene	5.55	-	4.9	7.54	2.5	1.8
Styrene	56.32	59.1	45.3	53.06	39.9	65.8
Benzene, (1-methylethyl)-	0.24	-	0.7	1.019	0.4	0.4
alpha.-Methylstyrene	1.71	-	6.3	6.49	6.8	7.7
Benzene, 1,1'-(1,3-propanediyl)bis	0.00	-	0.5	-	1.5	3.5
Other	25.58	40.7	37.2	25.2	45.5	14.9

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