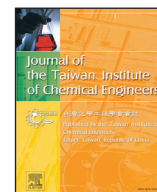




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# Metal decorated montmorillonite as a catalyst for the degradation of polystyrene

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## ABSTRACT

Benefiting a renewable source of precious hydrocarbons and getting rid of a huge environmental pollutant like polystyrene is the cry of the day. Waste polystyrene (PS) represents a source of valuable chemical products like styrene and other aromatics. Therefore, metals decorated montmorillonite (Mt) catalysts were prepared using Mg, Zn, Al, Cu and Fe and were evaluated for the tertiary recycling of waste polystyrene. The metal decorated catalysts characterized by N<sub>2</sub> adsorption/desorption, XRD & SEM techniques. 20% Fe/Mt and 5% Al/Mt were found with high activity for the production of liquid products and good selectivity for the production of low molecular weight aromatic products like styrene, toluene and ethylbenzene, etc. The yield of toluene, ethylbenzene, styrene and  $\alpha$ -methylstyrene was 8.49 wt.%, 5.13 wt.%, 49.28 wt.% and 2.80 wt.%, respectively using 5% Al/Mt catalyst and it was 10.15 wt.%, 6.42 wt.%, 50.93 wt.% and 2.31 wt.%, respectively using 20% Fe/Mt catalyst. The results showed that among the metal decorated Mt catalysts used, 5% Al/Mt and 20% Fe/Mg were found to be the most effective catalyst for selective conversion into aromatics. The products contained styrene monomer as a major along with toluene, ethylbenzene and  $\alpha$ -methylstyrene value added products. Thus, it was possible to demonstrate the feasibility of catalytic degradation as an alternative technology for the chemical recycling of waste PS.

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## 1. Introduction

The ongoing growths of population and rapid industrialization have led to the refusal of huge quantities of solid wastes on daily basis [1]. Municipal solid waste comprises a large proportion of styrene based plastics [2]. Plastics are recycled using five different ways, i.e., disposing by landfill, mechanical recycling, biological recycling, thermal incineration and chemical recycling [3]. Like other plastic, polystyrene (PS) is also non-biodegradable and their disposal depletes landfill sites. The incineration of these wastes produces toxic gases causing different health problems, including cancer, therefore, prohibited by public opinion [2,4–8]. Mechanical recycling is expensive and often full of impurities while biological recycling is much slow process and it is only practiced for degradable plastics. All the mentioned methods are not suitable for waste management. The best option is chemical recycling or tertiary recycling to get maximum benefit of the plastics waste and convert it into valuable hydrocarbons [3]. The tertiary recycling is achieved by three different means; (i) depolymerization,

(ii) partial oxidation and (iii) degradation or cracking or pyrolysis. Depolymerization cannot be applied to more than 70% of municipal solid wastes [9]. Partial oxidation is the direct combustion of polymer waste with high calorific value for energy recovery [9]. Therefore, the third method which includes catalytic degradation is the best option to be used because it does not require high temperature or costly conditions as needed for thermal degradation, biodegradation or photodegradation [9–11].

Proper selection or development of a catalyst enables us to get improved and selective products that not only yield desirable products, but also decrease the production cost [12]. Mostly, for the degradation of PS solid acid and base catalysts are used. The solid acid catalysts include zeolites, silica-alumina (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>), FCC, MCM-41, HZSM-5, mordenite, clinoptilolite, etc., while the solid base catalysts include magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), titanium dioxide (TiO<sub>2</sub>), potassium oxide (K<sub>2</sub>O), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), chromium oxide (Cr<sub>2</sub>O<sub>3</sub>), cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), zinc oxide (ZnO) and copper oxide (CuO), etc. These catalysts have been reported with high yield of liquid products having styrene monomer as the major product, but the reaction conditions used were economically not feasible and the selectivity of component products were also low with maximum number of undesirable products [13–21]. In order to increase the yield of

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liquid products with good selectivity of desirable products, novel impregnated catalysts were used for the degradation of PS [22]. Some researchers have degraded PS with modified or promoted catalysts but limited data is available with impregnated catalysts in the literature. Acid-treated halloysite clays were used by Tae et al., [23], they found that ethylbenzene was increased with the increase of contact time and acidity of catalyst, where high temperature increased styrene monomer. Better activity was found by Xie et al., [24] with modified silicon mesoporous molecular sieve as catalyst. Kim et al., [25] used modified alumina support with Fe, K, Ba, Zn and Mg catalysts for the degradation of PS and found Fe-K/Al<sub>2</sub>O<sub>3</sub> the best catalyst with a significant amount of liquid. The use of modified, or treated catalysts have brought significant increase in the activity and selectivity of the products, therefore, suggests the need for more advance catalysts (supported catalysts) more specifically impregnated catalyst. Impregnated catalysts can be prepared with the selection of proper active metal center (a precursor) over a suitable support [26] like silica, alumina, and activated carbon, etc. Mineral clays like montmorillonite (Mt) in the field of catalysis have got much interest and have been used for various purposes due to their high porosity, exchangeable cations and swellable properties. Mt is one of the important clay minerals that has widely used as supporting material [27–30].

In the present work a series of metal decorated catalysts were prepared over Mt support with Mg, Zn, Al, Cu and Fe as the active metal centers. The aim of the current study was the improvement of catalytic activity in terms of liquid products as well as the selectivity of component products.

## 2. Experimental

### 2.1. Materials

The polystyrene (PS) samples used have an average molecular weight (Mw) 200,000 g/mol purchased from Sigma-Aldrich. Montmorillonite (Mt) clay was obtained from a local research laboratory. MgCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O were purchased from Merck KGaA 64271, Darmstadt, Germany. AlCl<sub>3</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O were purchased from BDH Laboratory Supplies, Poole, BH151TD, England.

### 2.2. Catalyst preparation

Different concentrations of salts of Mg, Zn, Al, Cu and Fe, *i.e.*, (MgCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, AlCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O) were calculated as 5%, 10%, 15%, 20% and 25% on the basis of metal weight for a known weight of Mt. The relevant salts were impregnated over Mt support using the wet impregnation method. The active metal center salt was dissolved in appropriate amount of water and was poured into the slurry of Mt support and stirred the mixture for 1 h at 60 °C, filtered, washed with distilled water and dried in oven at 110 °C for 6 h. The catalyst sample was then calcined at 300 °C for 4 h and cooled in a desiccator. The dried sample was ground to powder and screened to a particle size ≤445 μm.

### 2.3. Catalyst characterization

Surface Area Analyzer NOVA2200e Quantachrome, USA was used for the determination of BET surface area of the prepared catalysts using N<sub>2</sub> adsorption/desorption at 77.4K. The morphology of catalysts was determined using Scanning Electron Microscope (SEM) JSM5910, JEOL, Japan instrument. X-ray diffraction (XRD) patterns were taken using a JDX-3532 JEOL (Japan) diffractometer with monochromatic Cu-Kα radiation (λ = 1.5418 Å) at 40 KV and 30 mA in the 2θ range of 10–80° with 1.03° per minute.

**Table 1**

BET Surface area for metal decorated catalysts using Mt as supporting material.

Catalysts	Surface area (m <sup>2</sup> /g)		Pore size (Å)	Pore volume (cc/g)
	BET	BJH		
<b>Mt</b>	116.21	489.23	115.39	1.25
<b>20% Mg/Mt</b>	96.14	412.08	121.84	1.26
<b>20% Zn/Mt</b>	78.25	297.6	102.38	0.68
<b>05% Al/Mt</b>	102.20	264.56	118.96	1.23
<b>15% Cu/Mt</b>	49.86	54.6	78.73	0.09
<b>20% Fe/Mt</b>	69.53	77.53	77.72	0.13

### 2.4. Catalyst activity

Polystyrene degradation experiments were conducted at atmospheric pressure in a Pyrex glass reactor (height 22 cm and internal diameter 7 cm) set in a heating assembly operates up to 1000 °C. PS (5 g) was degraded with the mixture of appropriate amount of relevant catalysts (weight by weight blend) for a constant period of time. The degradation experiments were run with virgin PS and heterogeneous catalysts without the use of any solvent and other additives. The degradation products, *i.e.*, liquids and gases were collected after condensation and measured. The residue left in the reactor was weighted and the products were expressed in terms of wt.% of the PS degraded.

### 2.5. Analysis

GC/MS analysis of the degraded products was performed with Shimadzu QP2010 Plus GC/MS. The instrument was fitted with 30 m capillary column, 0.25 mm internal diameter having DB-5MS (95% dimethylpolysiloxane, 5% polyphenyl) fused silica capillary column with 0.25 μm film thickness. Helium gas (99.99%) was used as carrier gas with a flow rate of 1.5 mL/min, sample injection volume was 1 μL and the injector port was provided with split mode (1:50). The injection temperature was 300 °C and the oven temperature was programmed as follow; initial oven temperature 35 °C (5 min), ramped at 5 °C/min to 100 °C (1 min), then ramped at 10 °C/min to 150 °C (10 min) and finally ramped at 2.5 °C/min to 290 °C (10 min). The ion source temperature used was 280 °C and interface temperature was 290 °C. The spectra were compared with GC/MS updated library for the identification of component products.

### 2.6. Catalyst activity studies for the degradation of PS

The catalytic activity of catalysts was tested in two phases as in our previous work [31]. In the first phase the Mt support was used as a catalyst and was employed in the process of PS degradation with the effect of degradation temperature, reaction time and feed to catalyst ratio. The selection criterion for optimum reaction conditions was based on maximum production of liquid products as well as total products. In the second phase, the prepared metal decorated catalysts over Mt support were evaluated. The catalytic activities of metal decorated catalysts were tested with the effect of percentage (%) of the impregnated metal using the same reaction conditions as used for Mt support alone.

## 3. Results and discussions

### 3.1. Catalyst characterization

Surface area, pore volume and size were calculated for all the prepared metal decorated catalysts over Mt support in comparison to Mt support (Table 1). The BET and BJH surface area of all

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