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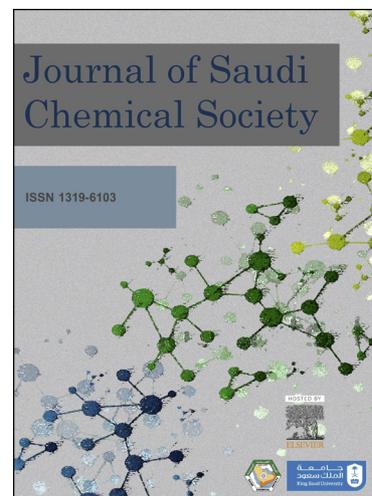
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Renewable Aromatics from the Degradation of Polystyrene under Mild Conditions

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A bimetallic FeCu/alumina catalyst was prepared and characterized. It showed excellent catalytic activity to quantitatively convert polystyrene (PS) into aromatics at low temperatures. A clear goldish yellow liquid was produced at 250 °C in a batch reactor without distillation. A liquid yield of 66% in an inert environment was achieved without the formation of coke and gas by-products. An exposure time of 90 min. and a catalyst loading of 200 mg were considered as an optimum condition to minimize the styrene re-polymerization. The gas chromatography/ mass spectrometry (GC/MS) analysis confirms that the primary products are styrene, ethylbenzene, cumene, toluene and α -methylstyrene.



Keywords: Polystyrene, bimetallic, low-temperature, catalytic degradation

1. Introduction

Plastic products play an important role in the modern life. As their production has increased to meet the market demand, their waste accumulation has created a serious environmental issues. Polystyrene (PS) represents 10 wt. % of the total plastic waste in which 15 million tons of PS is produced annually since 2008 [1,2]. There are four primary practices to handle the waste plastics, including landfilling, incineration, mechanical, and chemical recycling [3-6]. Currently, the oceans, seas, and rivers serve as sinks for the PS as well as other plastics debris [7]. PS represents 70% of overall marine debris plastics due to its poor recycling rate [7]. In fact, styrene monomer and other chemicals can leach out and get ingested by the marine life to eventually

impact our food [8]. Importantly, such chemicals can be impregnated in the beach sands as well. Kwon and co-workers have collected different beach sand and seawater samples from Pacific Ocean, Alaska and Hawaii and showed that all the samples contained styrene monomer and dimer which are carcinogenic [9].

As polystyrene has high energy content, chemical and thermal degradation of PS are the best recycling approaches. It has been reported that exposing PS to high temperatures can generate high yields of styrene as illustrated by Nishizaki and co-workers [10]. In this process, the C-C bonds are cleaved via radical pathways [11]. However, the thermal depolymerisation at high temperature results in the coke formation, and

consequently, a heat transfer limitation takes place [12]. The catalytic degradation of PS is thus favoured as it may offer advantages such as minimizing the reaction temperature and/or enhancing the selectivity. Indeed, different metals have been used, including Fe [13], Cu [14], Mg [15,16], Zn [17], Ni [18] and Pt [19], and supporting materials, such as alumina [20], HZSM-5 [21], TiO₂ [22] and silica-alumina [23], were employed to enhance the surface area, to improve metals dispersion, and to increase the thermal stability. Yet, the catalytic degradation still requires high reaction temperatures to obtain good conversion, and to adjust selectivity. At low temperatures (240-300 °C), negligible liquid products formation was reported. Marczewski and co-workers have shown that the degradation of PS below 300 °C only resulted in a slight reduction of the PS molecular weight [17,20,24].

As the chemical industry is now shifting the gears towards reducing overall energy consumption and the demand on styrene and ethylbenzene is increasing, an energy-efficient and economical catalyst that can give high liquid yields at low reaction temperatures is highly desirable. Herein, we report a full conversion of PS using the bi-metallic FeCu/Al₂O₃ in an inert environment. Neither gases nor coke were formed at 250 °C in the batch condition.

2. Experimental Details

2.1. Materials

Alumina (Al₂O₃), Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), Cupric nitrate trihydrate (Cu(NO₃)₂·3H₂O), and PS tablets with an average molecular weight (*M_w*) of 100,000 g/mol were purchased from Sigma-Aldrich and used without further treatment. The PS samples were crushed to be in the particle size range of 0.5 to 0.8 mm before the degradation reaction to enhance the contact with the catalyst. Specific solvent samples of HPLC grade were used for GC/MS calibration.

2.2. Catalysts preparation

2.2.1. FeCu over Al₂O₃ preparation

Alumina slurry was sonicated for 10 min and loaded with different metal precursors of both iron and copper by the wet successive impregnation technique. Each mixture was stirred at 60 °C until the water evaporated, and then dried in a vacuum oven at 110 °C for overnight. Finally, the FeCu/Al₂O₃ catalyst was calcined at 350 °C for 4 hours.

2.3. Catalyst characterization

The BET surface areas of the impregnated catalyst as well as the blank alumina were measured by surface area and porosity analyzer ASAP2420 Micrometrics using nitrogen adsorption and desorption at 77.4 K. The metal oxides distribution among the alumina surface was indicated by scanning transition electron microscopy (STEM)/ electron energy loss spectroscopy (EELS) (Figure. 1). The surface morphology of the impregnated

catalyst was determined by scanning electron microscopy (SEM) (Figure. 2). In addition, the energy-dispersive X-ray spectroscopy (EDS) was used (Figure. S1). The catalyst acidity was determined by NH₃-temperature programmed deposition. Briefly, 0.20g of each sample was weighted once at a time. The physisorbed water was removed by preheating each sample at 250 °C under a helium flow for 2 h. The reactor was then cooled down to room temperature followed by introducing ammonia into the reactor at 100 °C. After 1 h, the physisorbed ammonia was removed under the helium flow at 100 °C for 30 mins. Finally, the sample was heated from 100 to 600 °C at a rate of 10 °C/min. An on-line gas chromatograph with TCD detector was used to analyse the effluent gases.

2.4. Apparatus and analysis

Different pressures, catalyst: polymer ratios and reaction times were examined to achieve the optimized reaction conditions (Fig. S2). All the degradation reactions were conducted in a batch reactor. 2.0 g of polystyrene was used in all the reactions, and various amounts of the catalyst from 100 to 500 mg was. Polystyrene and the catalyst were well mixed in a 25 mL reactor vessel before heating. For all experiments, the reactor was purged with N₂ for 3 mins and the stirring speed was fixed at 400 rpm during all the reactions. The reactor was heated with the clamp-on band heater and the temperature was increased at 4 °C/min to 250 °C. The reaction was heated for additional 30-150 mins before being cooled down to room temperature. The resulting liquid was collected, filtered (ION Chrom Acrodisc membrane 0.45 μm) and characterized by gas chromatography /mass spectrometry GC/MS (Agilent.). The GC/MS was calibrated by using external standards (HPLC grade) including toluene, ethylbenzene, styrene, cumene, styrene dimers, and α-methyl styrene. The determination of the most resolved peaks was conducted via retention time and confirmed by the mass spectral library search. The response factors, from the five point calibration curves, were used to identify the weight of each compound. The GC/MS operating conditions are shown in Table 1. The remaining residue in the reactor was dissolved with toluene (5.0 – 10.0 mL). The catalyst was filtered and the toluene was removed in vacuo from the filtrate to give the oligomer mixtures, which were further dried in the vacuum oven at 50 °C overnight until the weight became constant to give the yields of the remaining oligomer residue.

Table 1 Instrumental conditions for GC/MS

Instrumental Part	Condition
Instrument	Agilent J&W DB-200
Column	DB-200 (length 30 m x diameter 0.25 mm x particle diameter 0.25μm)
Carrier gas	Helium
Injection temperature	250 °C
Oven temperature program	60 °C (8 min hold) to 250 °C (15 min hold) with 8 °C min ⁻¹
Mass data acquisition	Full scan
Solvent delay	No solvent delay

3. Results and discussion

3.1. Catalyst characterization

Aluminium oxide usually has irregular shapes with various thickness due to the superposition in certain areas which making it difficult to achieve a clear and meaningful contrast. Therefore, a scanning transmission electron microscope (STEM)/ electron energy loss spectroscopy (EELS) maps were generated to show the distribution of the metal oxides on the support. The presence of the bi-metallic particles over the alumina surface was confirmed by scanning different regions of the catalyst (Figure. 1). The electron beam drift detector was implemented during the scan of each area to avoid the drift in the electron beam.

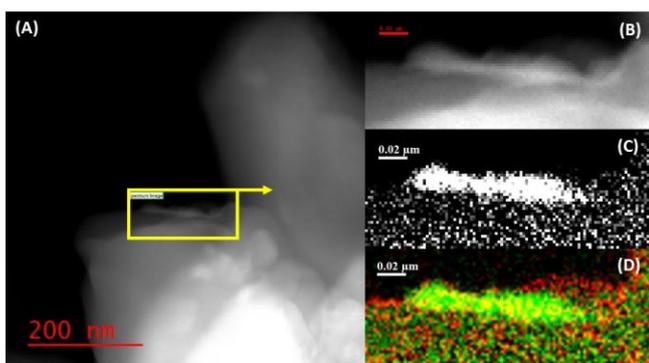


Figure 1. High magnification STEM/EELS chemical maps of Fe_2O_3 and CuO in $\text{FeCu}/\text{Al}_2\text{O}_3$ (A) STEM image of FeCu over alumina, (B-C) EELS maps of $\text{FeCu}/\text{Al}_2\text{O}_3$ (D) Coloured EELS map (the Iron oxide is represented by red colour and copper oxide is represented by green colour).

Scanning electron microscopy images show the alumina parent material before and after the loading of the bimetallic (Figure. 2). The BET surface area, BJH cumulative pore volume and Adsorption average pore width by BET of support and catalysts are given in Figure 2. The BET analysis shows that the catalyst is mesoporous with a low surface area. In addition, the decrease in alumina surface area after the deposition of the metal oxides indicates the successful loading of metal oxides into the alumina (Figure. S3).

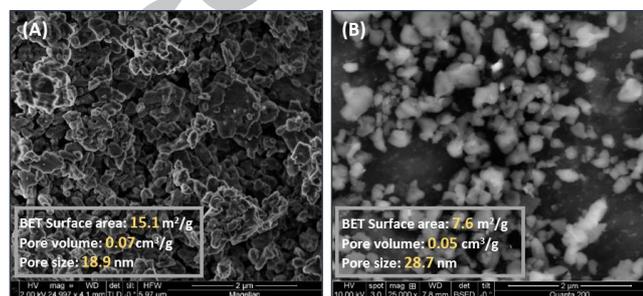


Figure 2. SEM images of (A) Parent material Al_2O_3 and (B) $\text{FeCu}/\text{Al}_2\text{O}_3$. The BET surface area, BJH cumulative pore volume and Adsorption average pore width by BET of the parent and $\text{FeCu}/\text{Al}_2\text{O}_3$ are in the left corners of each image.

3.2. Catalyst degradation activity

3.2.1. Effect of pressure

The PS degradation in the presence of the prepared catalyst was examined at $250\text{ }^\circ\text{C}$ for 90 min under N_2 . The degradation reaction in the absence of the catalyst was also conducted under the same condition for comparison. The use of $\text{FeCu}/\text{alumina}$ catalyst resulted in formation of a 66% liquid yield (Figure. 3). Noteworthy, the thermal degradation without the catalyst only resulted in a mixture of viscous oligomers. These observations indicate that the presence of the catalyst is essential for the effective PS degradation at $250\text{ }^\circ\text{C}$. $\text{FeCu}/\text{alumina}$ was then subjected to further investigation to identify the optimized conditions.

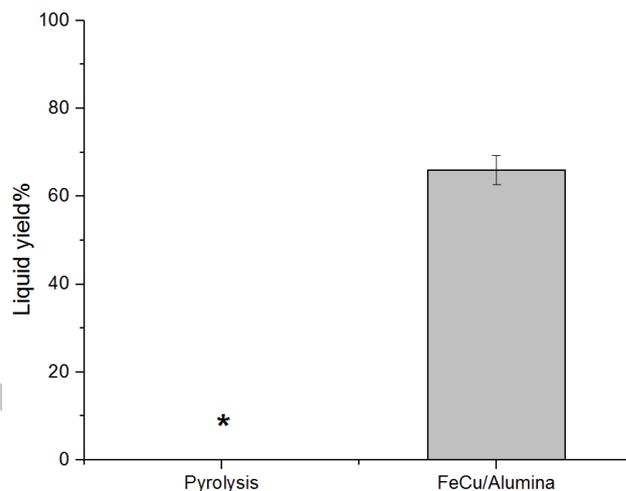


Figure 3. The comparison of liquid yield% using both pyrolysis and catalytic pyrolysis of PS using the bi-metallic catalyst (Degradation conditions: reaction time 90 min, temperature $250\text{ }^\circ\text{C}$, PS weight is 2.00g, catalyst loading 200 mg, N_2 0 psig) the start over pyrolysis denote production of oligomers only.

The effect of the pressure on the PS degradation was screened at $250\text{ }^\circ\text{C}$ under N_2 with pressures of 20, 40, 60 psi, respectively. No significant effect on the degradation performance and the products selectivity was observed (Figure. 4). In all cases, ethylbenzene was identified as the major product followed by styrene, which may suggest that the end-chain scission degradation reaction is a dominant pathway [25].

3.2.2. Reaction time dependence

The reaction time is one of the most important parameters that influence the efficiency of the PS degradation. There have been a limited number of studies on the reaction time effects in the literature [18, 19, 31-33]. As the decrease in the reaction time reduces the overall energy cost for the degradation reaction, a short reaction time is favoured as long as the efficient conversion is achieved. On the other hand, extending the exposure time increases the potential of further cracking of the liquid products into gases and the repolymerization of styrene under the batch condition. Consistent with these considerations, our data show that increasing the reaction time up to 90 min offers the highest liquid yield. Noticeable, styrene wt% decreases with increase the

exposure time as it tends to re-polymerise at low temperatures in the batch system (Figure. 5).

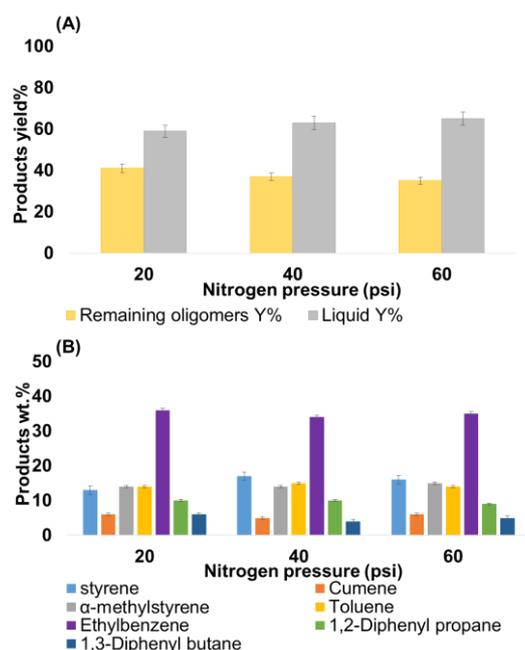


Figure 4. Pressure effect on 3FeCu/Alumina (Reaction conditions: temperature 250 °C, PS weight is 2.00g, catalyst loading 200 mg and reaction time 90 min)

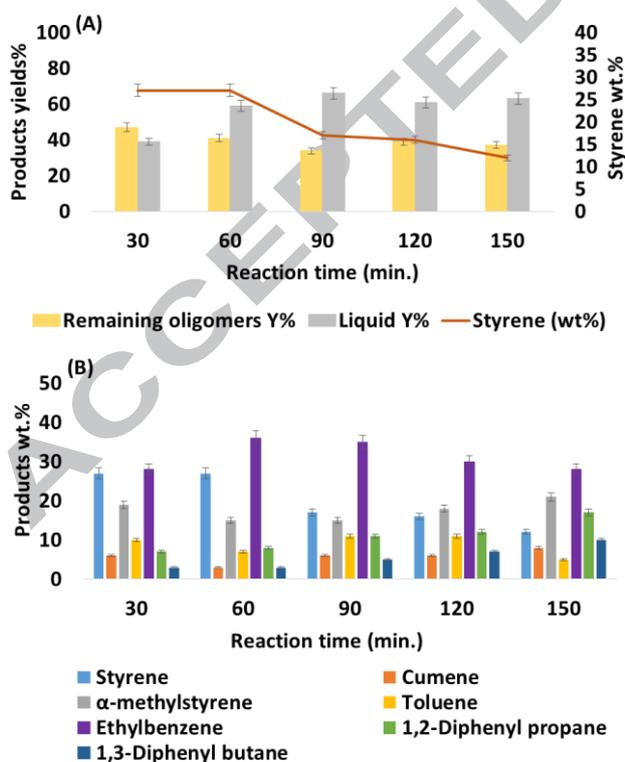


Figure 5. Effect of reaction time using the FeCu/Al₂O₃ catalytic system (Conditions: temperature 250 °C, N₂ pressure 0 psig and catalyst loading 200 mg).

3.2.3. Catalyst loading effect

The PS/catalyst ratio can be a crucial factor to the liquid yield and/or products selectivity. The PS degradation was thus further tested using different catalyst loadings from 100 mg to 500 mg per 2.00 g of PS. Increasing the amount of catalyst from 100 mg to 200 mg led to an enhancement in the liquid yield, but further increasing the loading to 300-500 mg resulted in lower liquid yields (Figure 6). These observations suggest the presence of secondary reactions, as styrene monomer tends to re-polymerize at 250 °C to form oligomer chains over the catalyst surface. The good balance between PS and the catalyst is key to achieve high conversion, liquid yields and improved products selectivity.

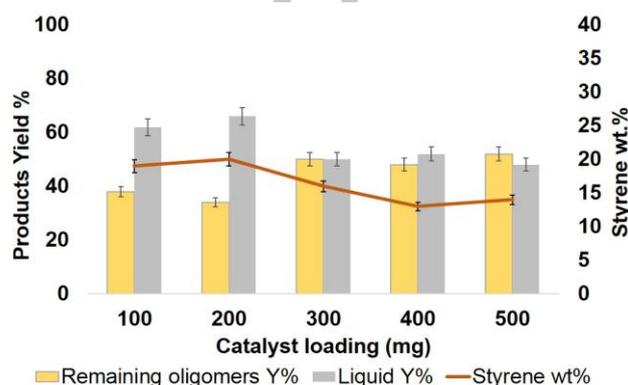


Figure 6. Catalyst loading effect (Degradation conditions: PS feed: 2.00 g, reaction time 90 min, temperature 250 °C, N₂ pressure 0 psig)

4. Plausible degradation pathways

The major products in the presence of the bimetallic catalyst are ethylbenzene, styrene, α-methyl styrene toluene, 1,2-Diphenyl propane (D1), 1,3-Diphenyl butane (D2), and cumene (Figure S4). Ojha and Vinu have recently reported the production pathways of different degradation products based on the acidic catalytic sites [26]. The NH₃-TPD results of our catalysts indicated the presence of weak and single acidic site (Figure. 7). We propose that in our system, the acidic site/proton attack on the phenyl group of PS may play a role. Presumably due to

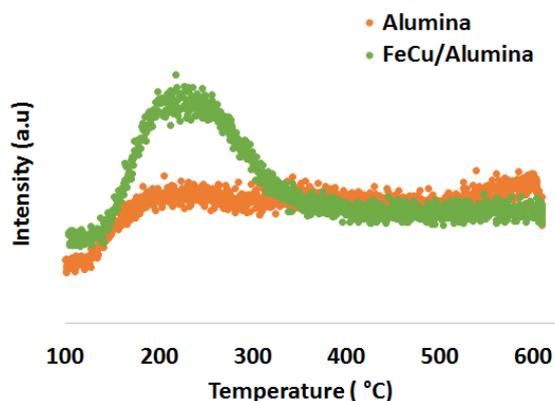


Figure 7. Temperature programmed desorption of ammonia before and after loading metals loading into Alumina.

the low degradation temperature, both the β -Scission and intramolecular radical shift reactions are both dominant reactions in our system. The β -scission is the most characteristic reaction which involves the end chain radical leading to the formation of styrene [27].

The presence of toluene may result from the the protonation of the PS phenyl group followed by β -Scission, while the formation of α -methyl styrene is due to the the intramolecular proton shift prior the β -scission [26]. Using the low surface area catalyst as well as low acidity is recommended to offer good styrene recovery and high liquid yields at this very mild batch reaction condition.

5. Conclusion

In summary, efficient PS degradation catalyzed by a Fe/Cu bimetallic catalyst has been achieved to give aromatic products under mild conditions. Different reaction parameters including pressure effect, catalyst loading and reaction time were screened. Full conversion of PS was obtained by employing FeCu/alumina at 250 °C. The balance between the exposure time, catalyst loading, surface area and catalyst acidity is important to reach the optimal liquid yield. The degradation process may involve both proton and radical initiated pathways which resulted in aromatics formation with no coke or greenhouse gases. Future work involving the degradation of polystyrene in an open system to enhance the liquid yields at this low temperature is ongoing and will be reported in due course.

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