

Waste Plastics to Liquid Fuels over Al-Impregnated Zeolite Beta Catalyst

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Abstract: 5wt% Al-impregnated zeolite beta catalyst is synthesized and characterized by well-known catalyst characterization techniques. A model municipal waste plastic mixture consisting of LDPE, HDPE, PP, and PS is hydrocracked over the catalyst. The experiments are performed in a high pressure autoclave reactor at three reaction temperatures, 360°C, 375°C, and 400°C and at cold hydrogen pressure of 20 bar. The feed to catalyst ratio is maintained at 20:1 (by weight). At 400°C, 95.7% conversion with 60.8% liquid yield is the result.

Key words: Waste plastics, chemical recycling, hydrocracking, hierarchical catalyst, zeolite beta.

1. Introduction

Each year the production of plastics is increasing, and it is increasing at a high rate. This enormous use of plastics is generating huge amount of plastic waste that needs to be recycled. The recycling of plastic waste not only decreases the burden on the environment, but it also capitalizes the potential resource of the waste. Chemical recycling methods such as thermal cracking, catalytic cracking, and hydrocracking can be applied to convert the waste plastic materials to liquid and gaseous fuels of high quality. Both thermal and catalytic cracking processes are endothermic in nature, whereas hydrocracking is an exothermic process. Hydrocracking requires lower temperature and produces better quality products with reduced quantity of olefins [1]. In hydrocracking hydrogen gas is used, most often in the presence of a catalyst to convert the long chain hydrocarbons to more useful smaller alkanes and aromatics.

In the present work, the hydrocracking of a model waste plastic mixture is carried out in the presence of an Al-modified zeolite beta catalyst. The experiments are performed at various levels of temperatures at fixed hydrogen pressure and fixed feed to catalyst ratio.

2. Experimental

2.1. Catalyst Preparation

5% (by weight) of aluminum was impregnated over the zeolite beta powdered catalyst (CP811C-300, Zeolyst International), coded here as B300. A calculated amount of aluminum nitrate nanohydrate ($\geq 98\%$, Sigma Aldrich) was added in 40 ml of water. 5 g of the beta support was mixed with this solution and

allowed to stir vigorously for 1 h at 50°C. The solution was then equilibrated for further 24 h at room temperature. The final aluminum impregnated zeolite catalyst was rinsed with water, dried in an oven at 100°C, and calcined at 600°C for 4 h at the rate of 2°C/min, in a muffle furnace. The final catalyst was named as BA1. The catalyst was then characterized using SEM, TEM, N₂-BET, wide angle XRD, and Py-FTIR techniques. The details about the procedures of the characterizations are given in Munir and Usman [2].

2.2. Activity Tests

The experiments were performed in 500 mL Parr autoclave reactor. 10 g of plastic material (40wt% HDPE, 10wt% LDPE, 30wt% PP, and 20wt% PS) and 0.5 g of catalyst were charged in the reactor and the reactor was closed thereafter. 20 bar hydrogen pressure was given at this stage and the temperature of the reactor was raised to the reaction temperature. 60 min residence time, at the set reaction temperature, was provided for the hydrocracking reaction to occur. The reactor was then cooled and the yields of gas, oil (n-heptane solubles), liquid (THF solubles), and the dried residue were measured. The conversion was defined on the basis of the THF insoluble dried residue. The detail of the experimental procedure is given in Munir and Usman [2].

3. Results and Discussion

3.1. Characterization of Catalysts

The SEM micrograph, displayed in Fig. 1, shows that the morphology of the Al-impregnated zeolite beta (BA1) is observed to be similar to that of the parent zeolite beta, i.e., ball like individual particles that are characteristic crystals of zeolite beta [3]. However, in this catalyst some partial agglomeration is observed due to the aluminum impregnation.

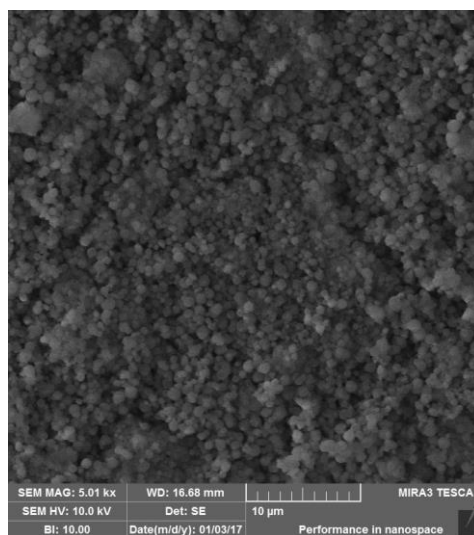


Fig. 1. SEM image of the Al-modified zeolite beta catalyst.

Fig. 2 shows the TEM image of the BA1 catalyst. It is observed that the definite crystalline structure of zeolite beta transformed into rough corrugated surface due to the addition of aluminum, bounded on the surface of the zeolite beta.

The results of N₂-BET characterization of the Al-modified zeolite beta are shown in Table 1 and Fig. 3. For comparison, Table 1 also shows the surface area and pore size information for the parent zeolite beta.

Fig. 3A demonstrates Type I isotherm that is a characteristic isotherm of the microporous zeolites [4]. The pore size distribution of the catalyst (Fig. 3B) shows that the aluminum impregnated zeolite beta

catalyst has reduced amount of the micropores. The aluminum impregnation has caused to occupy some spaces in the micropores of the zeolite beta and therefore resulted in a decrease in the microporous volume.

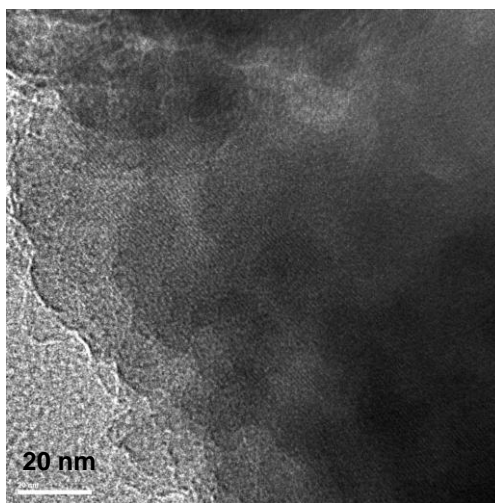


Fig. 2. TEM image of the Al-modified zeolite beta catalyst.

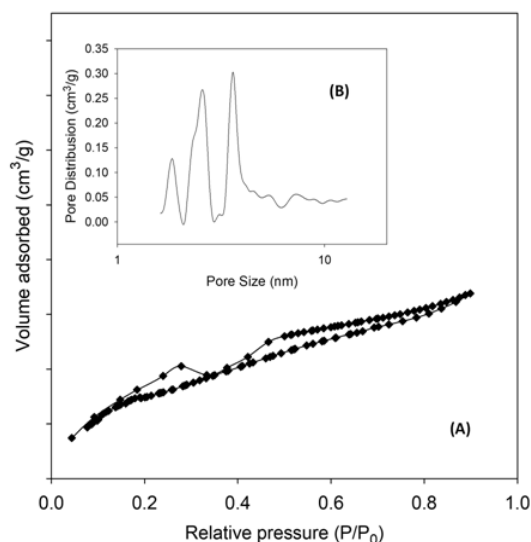


Fig. 3. N₂-BET characterization of the Al-modified zeolite beta: A) adsorption-desorption isotherm, B) Pore size distribution.

The wide angle XRD results of BAl are shown in Fig. 4. The observed diffraction pattern shows that after the impregnation of aluminum, the crystallinity of the zeolite beta is little affected and the diffraction pattern is close to that of the parent zeolite beta. The Py-FTIR of the catalyst shown in Fig. 5 depicts a band at about 1540 cm⁻¹ assigned to Brønsted acid sites [5]. A band at 1616 cm⁻¹ shows the presence of Lewis sites.

3.2. Hydrocracking Reactions

The results of the hydrocracking experiments over Al-modified zeolite beta are shown in Table 2. It can be seen that the conversion of the plastic mixture increases with an increase in temperature. It is increased from 43.6wt% to 95.7wt% when temperature is increased from 360°C to 400°C. At each temperature, the liquid yield is about two times higher than the gas yield. These are encouraging results as the liquid fuels are more desirable than the gaseous fuels in the economic sense.

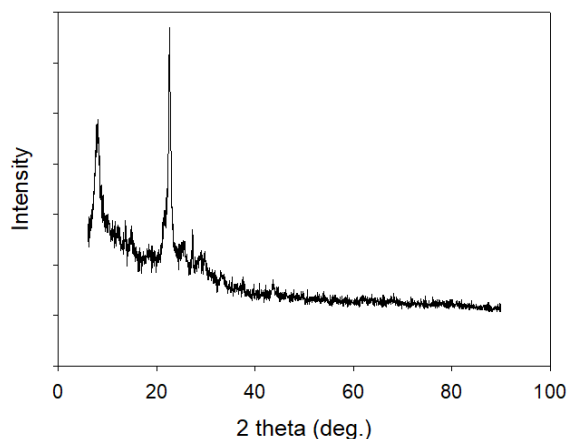


Fig. 4. Wide angle XRD of the Al-modified zeolite beta catalyst.

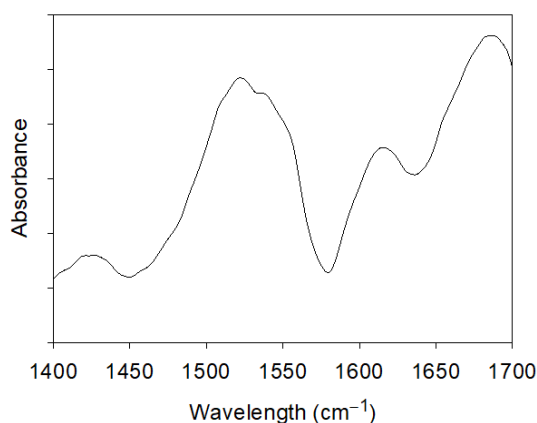


Fig. 5. Py-FTIR of the Al-modified zeolite beta catalyst.

The GC results with the oil portion (n-heptane solubles), at each temperature, reveal that a significant amount of gasoline is produced. However, it is observed that the concentration of gasoline is not affected by the reaction temperature. The increased amount of gasoline might be the cause of microporous nature of the aluminum impregnated zeolite beta catalyst. In other words, small pores are shape-selective towards the lighter components.

 Table 1. N₂-BET Results of the Catalysts

Catalyst	S_g (m ² /g)	S_m (m ² /g)	S_{BJH} (m ² /g)	$v_{p,m}$ (cm ³ /g)	$v_{p,BJH}$ (cm ³ /g)	$d_{p,BJH}$ (nm)	Ref.
B300	581.9	465.4	43.44	0.210	0.0465	3.23	[3]
BAI	499.5	430.9	41.89	0.198	0.045	3.24	This study

Table 2. Experimental Results of Activity and Selectivity over the Al-Modified Zeolite Beta Catalyst

T (°C)	X (wt%)	Y_{Gas} (wt%)	Y_{Oil} (wt%)	Y_{Liq} (wt%)	Y_{C5-C12} (wt%)	$Y_{C13-C18}$ (wt%)	Y_{C19+} (wt%)
360	43.6	15.8	18.9	24.6	49.9	33.0	17.1
375	77.7	25.0	45.8	47.5	55.5	20.2	24.3
400	95.7	29.1	60.4	60.8	55.5	21.7	22.8

S_g is surface area by using BET method, S_m is micropore area obtained by t -plot, S_{BJH} is BJH adsorption cumulative surface area of the pore between 17Å and 3000Å width, $v_{p,m}$ is micropore volume obtained by t -plot, $v_{p,BJH}$ is BJH adsorption cumulative volume of the pore between 17Å and 3000Å width, and $d_{p,BJH}$ is

BJH adsorption average pore diameter.

T is temperature, X is conversion, and Y stands for yield. 500 mL reactor vessel, feed to catalyst ratio is 20:1 (by wt.), cold H_2 pressure equals to 20 bar, and 60 min residence time.

4. Conclusion

The characterization results show that the aluminum impregnation of the zeolite beta only slightly affects the microporous nature of the zeolite beta. The Al-impregnated zeolite beta closely resembles in properties to the parent zeolite beta. The catalyst has shown reasonably good ability to crack the plastic materials and it has also shown favorable selectivity towards the production of lighter products such as gasoline. However, high gas yields are also obtained.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The first author analyzed the data and wrote the article while the second author did the experimental work and also analyzed the data. Both authors had approved the final version.

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Muhammad Rashid Usman had his PhD in chemical engineering and analytical science from The University of Manchester, Manchester, and MSc and BSc in chemical engineering both from University of the Punjab, Lahore.

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