Synthesis and characterization of mesoporous hydrocracking catalysts

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Abstract. Mesoporous catalysts have shown great prospective for catalytic reactions due to their high surface area that aids better distribution of impregnated metal. They have been found to contain more adsorption sites and controlled pore diameter. Hydrocracking, in the presence of mesoporous catalyst is considered more efficient and higher conversion of larger molecules is observed as compared to the cracking reactions in smaller microporous cavities of traditional zeolites. In the present study, a number of silica-alumina based mesoporous catalysts are synthesized in the laboratory. The concentration and type of surfactants and quantities of silica and alumina sources are the variables studied in the preparation of catalyst supports. The supports prepared are well characterized using SEM, EDX, and N2-BET techniques. Finally, the catalysts are tested in a high pressure autoclave reactor to study the activity and selectivity of the catalysts for the hydrocracking of a model mixture of plastics comprising of LDPE, HDPE, PP, and PS.

1. Introduction
In the past few decades, there has been a massive increase in the demand of plastics worldwide, in all sectors of industry and also in daily life. The production of plastic products are increasing day by day due to its light weight, durability, low cost, low degradation rates, and good insulating properties. This huge plastic production results in the generation of gigantic plastic waste. About 25% of all the solid waste comprised of plastics. These plastic wastes are treated by the popular waste management techniques that include landfilling, incineration, and recycling. Landfilling of plastics is not a valued method of waste disposal. Plastic waste occupies a huge volume of landfill for a longer time due to its slow degradation rate. Moreover, the plastic waste in a landfill is a source of many environmental hazards. Incineration of plastic waste, for getting energy, results in the emission of poisonous gases that are unacceptable from the environmental point of view. Feedstock recycling or chemical recycling for waste plastics is highly encouraged all over the world. It includes chemical depolymerization to monomers, gasification, pyrolysis, catalytic cracking and reforming, and hydrocracking [1]. Compared to the other chemical recycling methods, hydrocracking of waste plastic into liquid fuels is highly advantageous process. The fuel obtained as the result of pyrolysis and catalytic cracking is highly unsaturated and found unfit to be used as engine fuel [2]. However, high quality liquid fuel is obtained as the result of waste plastic hydrocracking. Hydrocracking of waste plastic requires a dual-functional catalyst that has a hydrogenation-dehydrogenation function as well as acidic function [3]. Microporous acidic zeolite supports such as HZSM-5 [1, 4-12]and HY [4, 12, 13] have been used by many researchers and resulted in appreciable conversions. However, most of the converted product...
comprised of gases and a rather small quantity of liquid was obtained due to the microporous cavities of zeolites that hinder diffusion of larger molecules of plastics. On the other hand, the role of mesoporous supports for waste plastic hydrocracking has been studied by only a few investigators. Mesoporous catalysts are expected to demonstrate great prospective for hydrocracking reactions due to their high surface area, that aids better distribution of the impregnated metal, and larger pore distribution. Mesopores in these catalysts allow the diffusion of heavy molecules and result in the production of more liquid fuel as compared to gaseous product. The only shortcoming of mesoporous catalysts is their weak acidic character. In the present study, mesoporous catalysts that contain strong acid sites are synthesized by novel methods. These catalysts contain the acidity along with mesoporosity required for the hydrocracking of heavy molecules like polymers. The aluminum is incorporated during the gel formation in a direct synthesis approach. Different Si/Al ratios are used and their effect on the hydrocracking of a model waste plastic mixture is investigated.

2. Experimental

2.1. Materials

Model waste plastic feed used for the hydrocracking reactions is a mixture of virgin high density polyethylene (HDPE, \( d = 0.952 \text{g/cm}^3 \)), low density polyethylene (LDPE, \( d = 0.918 \text{g/cm}^3 \)), polypropylene (PP, \( MW = 250000, d = 0.9 \text{g/cm}^3 \)), and polystyrene (PS, \( MW = 192000 \)). Tetraethylorthosilicate (TEOS, 98% purity), sodium hydroxide, aluminum isopropanoxide (≥98% purity), HCl (35.4% purity), F127, cetyltrimethylammoniumbromide (CTAB, ≥99% purity), and tetrapropyl ammonium bromide (TPAB) are used in the synthesis of catalysts. Apart from HCl (35.4% purity) and NaOH, all the chemicals were purchased from Sigma-Aldrich and used without any further purification. All the solutions are made in a double distilled water.

2.2. Catalyst preparation

2.2.1 Al-SBA16(10) and Al-SBA16(20)

In a typical procedure F127 was dissolved in 2.0 M HCl with continuous stirring for 1.0 h at room temperature. Afterwards, 6.0 g of TEOS was added into it. The mixture was hydrolyzed with vigorous stirring for 4 h at 40°C. Then, a calculated amount of aluminum isopropanoxide was added for achieving Si/Al wt. ratio of 10. This solution was allowed to stir vigorously, overnight, to form ordered mesoporous structure. For hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 100°C in an oven for a complete day. The final product was centrifuged and washed several times with double distilled water. The catalyst was dried in oven for 20 h at 100°C. The catalyst was calcined for 6 h in a muffle furnace at 600°C where the temperature increased from room temperature to the calcination temperature at the rate of 2°C/min. The catalyst was named as Al-SBA16(10). Al-SBA16(20) was prepared with the same method with Si/Al wt. ratio of 20.

2.2.2 Mesoporous zeolite

Mesoporous zeolite was prepared by dissolving TPAB in double distilled water. After complete dissolution, TEOS was added into it. The mixture was hydrolyzed with vigorous stirring at room temperature. Aluminum isopropanoxide was added in calculated amount in 0.1 M NaOH solution for achieving Si/Al wt. ratio of 20. The two solutions were mixed together and stirred vigorously. After this, CTAB was dissolved into the solution at room temperature. The mixture resulted was again subjected to stirring. For hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 120°C in an oven for 2 days. The final product was centrifuged and washed several times with double distilled water. The catalyst was dried in oven for 20 h at 100°C. The catalyst was calcined for 5.0 h in a muffle furnace at 550°C. The catalyst was ion exchanged in order to achieve proton form. The catalyst was then filtered and washed with double distilled water and dried in an oven at 100°C for 12 h. The dried catalyst was calcined again at 550°C for 4.0 h in a muffle furnace. The catalyst was named as MZ-20.
2.3 Catalyst characterization

Scanning electron microscopy (SEM) of samples were obtained by using Field Emission Scanning Electron microscope. All images were obtained using samples coated with carbon (sputtering) to reduce the effects of charging. Energy Dispersive X-ray (EDX) spectroscopy was performed for elemental analysis to find out the elemental composition of the catalysts. Potential silica to alumina ratio was evaluated by using this technique. Micromeritics TriStar II-3020 (Surface Area and Porosity Analyzer) was used for N₂ adsorption/desorption isotherms of the catalysts at 77.3 K. All the samples were degassed under vacuum at 200°C for 2 h, by using Micromeritics Smart Prep (Programmable Degas System) before the measurement. The total pore volume was estimated from the analysis of nitrogen amount adsorbed at a relative pressure (P/P₀) of 0.9933 by assuming negligible adsorption on the external surface as compared to adsorption in the pores. For all the analysis, correlation coefficients of 1.0 were obtained. N₂-BET surface area was calculated by using Brunauer-Emmett-Teller (BET) method. Pore surface area and pore volume were estimated by t-plot method. Barrett-Joyner-Halenda (BJH) model was used for the calculation of pore size distribution using adsorption branch of the isotherm. The estimation of the size of a mesopore was carried out by using BJH procedure to the adsorption branch of the isotherm.

2.3 Activity tests

Catalysts activity is evaluated by using them for the plastic hydrocracking. A waste plastic model mixture is prepared with HDPE (40%), LDPE (10%), PS (20%), and PP (30%). Feed to catalyst ratio used for all the reactions is 10:5 by wt. The reactions are performed at 400°C with reaction time of 50 min. The reactions are carried out in a high pressure 600 mL SS autoclave reactor (Parr Instrument Co.) under initial H2 pressure of 20 bar at room temperature. After the reaction, the reactor is allowed to cool down. The gases are collected at room temperature. The remaining product obtained is solvent extracted in order to evaluate the yield of oil (n-heptane solubles), liquid (THF solubles), and solids (the THF insolubles containing catalyst, coke, and unreacted plastic remained after drying in an oven).

3. Results and discussion

Figure 1 (a-c) are representative SEM photographs of Al-SBA16(10) consisting of mesoporous SBA16 with Si/Al ratio of 10. The images show some irregular shaped particles with rough surfaces along with some randomly shaped particles, as is observed by the other researchers [15]. The surface is rough with marble like texture which seems to exhibit amorphous mesoporous phase.

Figure 1 (d-f) are the SEM photographs of Al-SBA16(20). The surface of the catalyst seems irregular. Aggregated spherical particles of small size could be seen along with the presence of some macrospheres. The loose aggregates of spherical particles may indicate the presence of mesoporous phase [14]. However, macrospheres are formed due to the higher silica content [15] in Al-SBA16(20) as compared to Al-SBA16(10). Figure 1 (g-i) are representative SEM photographs of MZ-20. The images show some loose aggregates along with some spherical as well as cubical particles. The loose aggregates found may indicate the presence of mesoporous MCM-48 phase [14]. The cubic particles seen, may demonstrate the presence of ordered zeolite structure. It is observed by the images that the cubic particles are interconnected with the mesoporous spherical aggregates, thus strongly support the concept of mesoporous zeolite structure formation.

Table 1 shows the Si/Al ratio of the gel and actual Si/Al ratio in the catalysts, as obtained from EDX analysis. It is found that the Si/Al ratios obtained from the EDX analysis are nearly the same as that of the gel. This could be attributed to their formation in neutral medium that inhibits the possible aluminium leaching.

Structural properties of the two composite catalysts are summarized in Table 2. BET surface area of Al-SBA16(10) and MZ-20 is higher than that of Al-SBA16(20). The mesoporous area, as is evaluated from BJH area of all the catalysts, is much higher than that of their corresponding microporous area. It shows the presence of large area with mesopores. The microporous area of MZ-
20 is higher than the microporous area of the other two catalysts. It shows that the catalyst is composite with micropores and mesopores.

Pore size distribution of catalysts is demonstrated in Figure 2. Al-SBA16(10) shows a narrow pore size distribution centered at 4 nm. Pore sizes are in the range of 2-32 nm. Al-SBA16(20) demonstrates bimodal pore size distribution at 4.5 nm and 11.5 nm. Both are in the mesoporous range. Pore size distribution of MZ-20 also shows a bimodal pore size distribution with most of the pore sizes are 5 nm in diameter. Pore sizes are in the range of 2-24 nm in that catalyst sample. Micropores of 2 nm are present and mesopores of up to 24 nm show their existence. Pore size distribution of MZ-20 confirms its composite structure with micropores and mesopores.

Table 1. Si/Al weight ratios in gel and that obtained by EDX analysis of different catalysts.

| Name of catalyst   | Si/Al (initial) | Si/Al (EDX) |
|--------------------|-----------------|-------------|
| Al-SBA16(10)       | 10              | 10.84       |
| Al-SBA16(20)       | 20              | 19.52       |
| MZ-20              | 20              | 20.36       |

Table 2. Structural properties of different catalyst samples

| Samples            | Surface area\[^a\] (m²/g) | Micropore area\[^b\] (m²/g) | BJH area | Micropore volume\[^d\] (cm³/g) | BJH volume\[^e\] (cm³/g) | BET Pore diameter\[^f\] (nm) | BJH Pore diameter\[^g\] (nm) |
|--------------------|----------------------------|----------------------------|----------|--------------------------------|---------------------------|-------------------------------|-------------------------------|
| Al-SBA16(10)       | 220.98                     | 5.81                       | 219.5    | 0.0030                         | 0.4866                    | 9.389                         | 8.868                         |
| Al-SBA16(20)       | 110.01                     | 5.65                       | 101.5    | 0.0033                         | 0.3426                    | 13.17                         | 13.51                         |
| MZ-20              | 239.50                     | 17.6                       | 205.9    | 0.0057                         | 0.6350                    | 11.32                         | 12.33                         |

\[^a\] Surface area by using BET method
\[^b\] Micropore area obtained by t-plot
\[^c\] BJH adsorption cumulative surface area of the pore between 17Å and 3000Å width
\[^d\] Micropore volume obtained by t-plot
\[^e\] BJH adsorption cumulative volume of the pore between 17Å and 3000Å width
\[^f\] Adsorption average pore dia (4V/A) by BET
\[^g\] BJH Adsorption average pore dia (4V/A)
The results of catalyst activity tests are shown in Table 3. The catalyst activity tests in high pressure autoclave reactor with model waste plastic mixture show that improved results of activity and selectivity are obtained with Al-containing SBA catalysts compared to micro-mesoporous catalyst, MZ-20, and no catalyst conditions. The minimum conversion and lower yield of oil are obtained using MZ-20 catalyst where the THF insolubles are the highest. For the two Al-SBA catalysts, the conversions are virtually similar but the higher oil is produced with Al-SBA16(20), a mesoporous catalyst having higher silica-alumina ratio and broader range of mesopores that may aid in the formation of higher yield of liquid fuel. Important to note is that the surface area of the MZ-20 is the highest among the catalysts, shown in Table 2, however, it has given the minimum oil yield while the surface area of Al-SBA16(20) is the minimum but it yields the maximum oil product though the Si/Al ratios of the two catalysts are similar. It may be concluded that pore size distribution is also a critical factor for obtaining the desired product yield.
Figure 2. Pore size distribution of Al-SBA16(10), Al-SBA16(20), and MZ-20 catalysts

Table 3. Results of hydrocracking of model plastic mixture

| Run | Catalyst used | Gas yield (wt%) | Oil yield (wt%) | Total liquid yield (wt%) | Solid yield (wt%) | Conversion (wt%) |
|-----|---------------|----------------|----------------|--------------------------|-----------------|------------------|
| 1   | No catalyst   | 12.9           | 13.0           | 22.2                     | 61.1            | 38.9             |
| 2   | Al-SBA16(10)  | 8.34           | 21.0           | 27.4                     | 59.7            | 40.2             |
| 3   | Al-SBA16(20)  | 3.89           | 26.3           | 31.0                     | 60.3            | 39.7             |
| 4   | MZ-20         | 4.97           | 12.0           | 21.0                     | 69.5            | 30.5             |

4. Conclusion
The characterization results of the catalysts have revealed the presence of mesopores in the catalysts and confirm the formation of composite structure of micro-mesoporous zeolites. A higher silica-alumina ratio results in the formation of macropores which is a characteristic feature of high silica containing mesoporous catalysts. Higher silica-alumina ratio catalyst, Al-SBA(16)20, shows larger pore diameter, slightly larger pore volume, and lower surface area and shows a bimodal pore size distribution compared to lower silica-alumina ratio catalyst, Al-SBA(16)10, which shows a unimodal pore size distribution. Al-SBA(16)10 gives the highest gas yield showing it has higher cracking activity characteristics whereas highest liquid yield is obtained over Al-SBA-16(20) with highest pore diameter. It is therefore concluded that silica-alumina ratio and pore size distribution are the key factors in determining the required activity and selectivity of a catalyst. Surface area solely does not seem to play decisive role in the cracking ability of a catalyst.
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