

## Research Article

# Catalytic Pyrolysis of Low Density Polyethylene Using Cetyltrimethyl Ammonium Encapsulated Monovacant Keggin Units ( $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ ) and ZSM-5

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The effect of the catalysts on the pyrolysis of commercial low density polyethylene (LDPE) has been studied in a batch reactor. The thermal catalytic cracking of the LDPE has been done using cetyltrimethyl ammonium encapsulated monovacant keggins ( $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ ), labeled as CTA-POM and compared with the ZSM-5 catalyst. GC-MS results showed that catalytic cracking of LDPE beads generated oilier fraction over CTA-POM as compared to ZSM-5. Thus, the use of CTA-POM is more significant because it yields more useful fraction. It was also found that the temperature required for the thermal degradation of LDPE was lower when CTA-POM was used as a catalyst while high temperature was required for degradation over ZSM-5 catalyst. Better activity of CTA-POM was due to hydrophobic nature of CTA moiety which helps in catalyst mobility and increases its interaction with hydrocarbons.

## 1. Introduction

Widespread use of nonbiodegradable plastic waste is a serious threat to environment. Its recycling is considered to be a useful option for the management of plastic wastes. Among various methods of plastic recycling, cracking is the most widely used method; however, it has a drawback of high energy consumption. Use of appropriate catalyst decreases the reaction temperature and produces valuable products of high quality. For polymer cracking reactions, solid catalysts have gained special attention in terms of environmental safety, in the past many years [1]. A variety of catalysts such as zeolites, FCC, aluminas, silica-alumina, aluminium pillared clays, mesostructured catalysts, and hybrid zeolitic-mesoporous materials have been used for catalytic cracking; however, the yield of valuable fuel is very low [2–5]. HZSM-5 has been found to produce better yield of products during pyrolysis of high-density polyethylene (HDPE); however, more gaseous fraction is produced compared to oilier fraction [6, 7]. Silica-alumina can produce higher yield of liquid fuel

and more valuable gas product but at high temperature (400 to 550°C) [8].

More recently, polyoxometalate (POM) has been reported to be a catalyst for cracking reactions. POMs are aggregates of negatively charged transition metals along with oxygen with an infinite variety of chemical and physical properties. They have an important property as their structure can be modified in a number of ways which makes them attractive to be used as a catalyst. POMs have been considered as a solid acid alternative because these materials have not only a high acidity (higher than zeolites) but also redox properties which lead to broader applications.

The present research demonstrated the application of the modified hexadecyl trimethyl ammonium (CTA) encapsulated lacunary keggins type POM (labeled as CTA-POM) for cracking of low density polyethylene and its comparison with ZSM-5 catalyst. Both POM and ZSM-5 are solid acid catalysts with strong Bronsted acid sites. ZSM-5 has been widely used in cracking process and other petrochemical applications [9–11]. However, there are very few reports on the use of POM

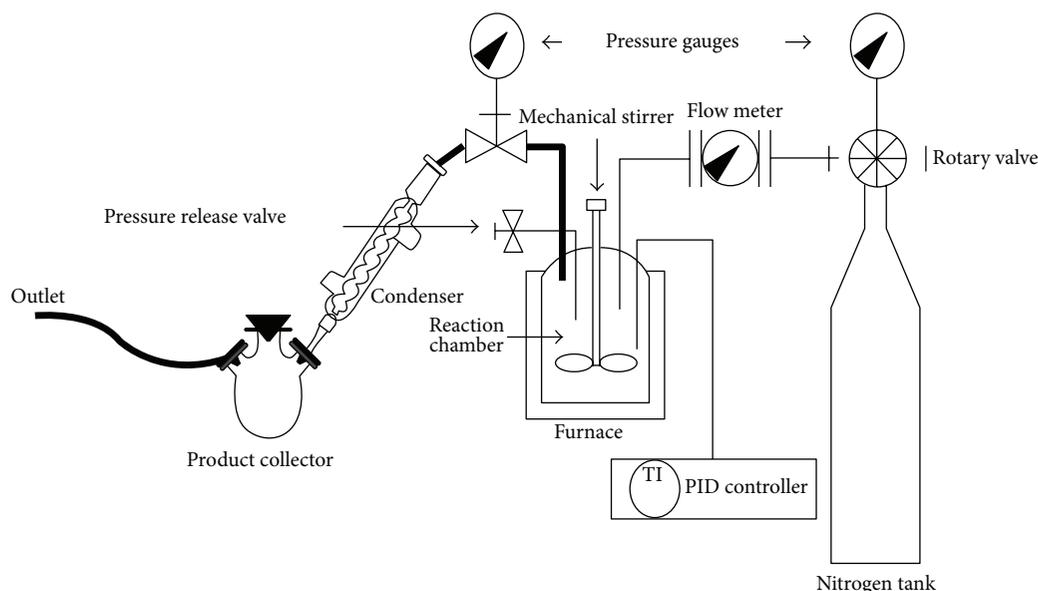


FIGURE 1: Schematic diagram of the reactor used for thermal catalytic cracking of LDPE.

for catalytic cracking. The purpose of incorporation of  $\text{CTA}^+$  was to facilitate the hydrophobic distribution of catalyst for less mass transfer resistance and faster reaction rate [12]. The results obtained showed that CTA-POM gives higher percentage of liquid fraction of hydrocarbons at relatively low temperature as compared to ZSM-5.

## 2. Material and Methods

**2.1. Materials.** Commercial low density polyethylene ( $M_w = 35000$ ,  $M_n = 7700$ ) beads were used in this study and obtained from market. ZSM-5 catalyst was obtained from Beijing University of Chemical Technology, China.

### 2.2. Methods

**2.2.1. Preparation of Catalyst Lacunary Keggin Type CTA-POM.** CTA-POM was prepared according to our previous reported [12] procedure. 9.1 mmol of  $\text{Na}_2\text{HPO}_4$  was mixed with  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (100 mmol) in 200 mL of water. The pH was adjusted to 4.8 by adding acetic acid dropwise. An aqueous solution of CTAB (45 mmol) in water (20 mL) was added dropwise with stirring at  $85^\circ\text{C}$ . The solid formed was filtered off and dried in vacuum at  $100^\circ\text{C}$ . The prepared catalyst  $(\text{CTA})_4\text{H}_3(\text{PW}_{11}\text{O}_{39})$  was labeled as CTA-POM.

**2.2.2. Thermal Catalytic Degradation of Low Density Polyethylene.** The effect of two different catalysts, CTA-POM and ZSM-5, on the pyrolysis of LDPE was studied. Thermal catalytic cracking was performed in a batch reactor made up of stainless steel (Figure 1). The reaction vessel was made up of stainless steel, placed inside a furnace which was controlled by a PID controller. The temperature was measured by a Cr-Al: K-type thermocouple placed inside the vessel. 10 g of LDPE beads and 0.1 g CTA-POM catalyst were added into the reactor.  $\text{N}_2$  gas was purged into the reactor to provide inert

atmosphere for cracking. Then reactor was heated at rate of  $5^\circ\text{C}/\text{minute}$  and the product was collected in a vessel attached at the end of water condenser. Total mass of oil was calculated by the following formula:

$$m = V \times \rho, \quad (1)$$

where  $m$  is mass of oil,  $V$  is volume, and  $\rho$  is density of oil. The mass of gas was calculated by subtracting the weight of liquid and wax from total weight used.

The liquid and wax product were analyzed by GC-MS technique (JEOL model JMS-A  $\times$  5050 H mass spectrometer; JEOL, Japan) combined with Hewlett Packard 5890 Gas Chromatograph (JEOL, Japan). The same experiment was repeated with ZSM-5 catalyst. Thermal catalytic pyrolysis of LDPE occurred between  $260$  and  $280^\circ\text{C}$  over ZSM-5 catalyst, while using CTA-POM the polymer was degraded at relatively lower temperature, that is,  $220$ – $240^\circ\text{C}$ . The reaction was completed in about 1.5 hours.

## 3. Results and Discussion

The degradation temperature of polyethylene depends upon the nature of the catalyst [13–15]. Thermal pyrolysis of LDPE in absence of catalyst took place at  $420^\circ\text{C}$ . Catalysts lowered the degradation temperature of polymer to below  $300^\circ\text{C}$ . Thermal catalytic pyrolysis of LDPE occurred between  $260$  and  $280^\circ\text{C}$  over ZSM-5 catalyst, while using CTA-POM the polymer degraded at relatively lower temperature, that is,  $220$ – $240^\circ\text{C}$ . The lowering of temperature might be associated with the availability of acidic protonic sites on catalyst. More protonic acidic centres are available at CTA-POM while in case of ZSM-5 limited contact of polymer with acidic sites takes place due to small microporous structure, as discussed by Gaca et al. [13]. In addition, it is supposed that CTA increases the lipophilicity of catalyst and increases

TABLE I: Percentage and nature of hydrocarbons with ZSM-5 and CTA-POM.

Catalyst	Carbon number	Nature of hydrocarbons	Percentage %
ZSM-5	C <sub>7</sub> -C <sub>16</sub>	Saturated (alkanes)	32.38
	C <sub>8</sub> -C <sub>13</sub>	Unsaturated (alkenes)	49.54
	C <sub>16</sub> -C <sub>18</sub>	Unsaturated (alkynes)	9.38
	C <sub>7</sub> -C <sub>10</sub>	Saturated cyclic (cycloalkanes)	8.69
POM	C <sub>8</sub> -C <sub>13</sub>	Saturated (alkanes)	57.68
	C <sub>8</sub> -C <sub>12</sub>	Unsaturated (alkenes)	32.86
	C <sub>8</sub>	Saturated cyclic (cycloalkanes)	3.02
	C <sub>7</sub> -C <sub>8</sub>	Unsaturated cyclic (cycloalkenes)	6.44

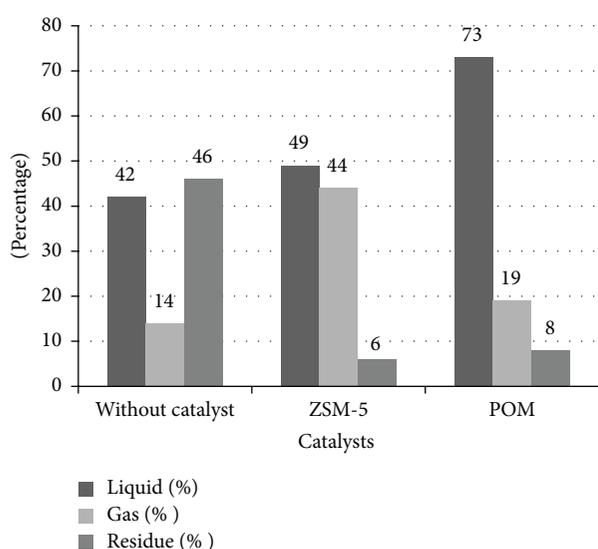


FIGURE 2: Product yield of degradation with and without catalyst.

its mobility; as a result, there is more interaction between catalyst and molten polymer hydrocarbons. These factors might affect the degradation temperature and lead to decrease in cracking temperature.

The experimental results showed that the rate of degradation of LDPE over catalysts was fast and the reaction was completed in almost 1.5 hours as compared to thermal pyrolysis which was accomplished in more than 3 hours.

**3.1. Product Yield of Degradation.** Figure 2 shows the percentage yield of liquid fraction obtained by catalytic degradation of LDPE over CTA-POM and ZSM-5. The percentage yield of liquid fraction was high, that is, 73 wt.% in case of CTA-POM with only 5 wt.% of solid residue. ZSM-5 produced large fraction of gaseous components (44 wt.%) and relatively less amount of liquid fraction. Similar results were obtained by Arthur et al. [16] for ZSM-5. The increase wt.% of liquid fraction with CTA-POM was due to the availability of more active sites and enhanced interaction between catalyst and polymer (due to CTA<sup>+</sup> component).

**3.2. Composition of Liquid Product.** The liquid fraction obtained by the catalytic cracking of LDPE over CTA-POM catalyst contains a significant amount (about 87%) of petrol-like hydrocarbons (C<sub>6</sub>-C<sub>12</sub>), while ZSM-5 catalyst produced ca. 57% C<sub>6</sub>-C<sub>12</sub> hydrocarbons.

Table 1 shows the type and nature of hydrocarbons in oil produced with ZSM-5 and CTA-POM as a result of polymer degradation. The mole percentage of saturated hydrocarbons (alkanes) in oilier fraction produced by cracking of LDPE over CTA-POM was much higher (52.57%) compared to liquid produced over ZSM-5 (32.38%) while mole percentage (%) of alkenes and cycloalkanes was the same for both catalysts. In oil produced after catalytic cracking of polymer over CTA-POM, both saturated and unsaturated cyclic compounds were present. According to Ng et al. [17], the presence of higher amount of paraffins and aromatic compounds is an indication of formation of olefins as intermediate in oil fraction which are very reactive and readily convert into paraffins and aromatics. Therefore, it is supposed that large amounts of olefins, as intermediate, are produced over CTA-POM catalyst which reform to generate alkanes and aromatic compounds.

The formation of higher percentage of alkanes over CTA-POM catalyst is supposed to be due to its protonic acidic centres at its surface and organic group hexadecyl trimethyl ammonium encapsulating POM, while in case of ZSM-5 due to small pore size limited contact of polymer with acidic sites of catalyst takes place, as discussed by Gaca et al. [13].

Figure 3 shows the distribution of hydrocarbons in oil formed over ZSM-5 catalyst. It is clear from the table that ZSM-5 produced higher percentage of olefins as compared to paraffin. Among these hydrocarbons, the mol. percentage of C<sub>12</sub> olefin was highest, while there were few hydrocarbons in the range of C<sub>13</sub> to C<sub>18</sub>. However, maximum amounts of C<sub>6</sub>-C<sub>12</sub> were present in oil which are components of petrol oil.

Figure 4 shows the percentage distribution of hydrocarbons (alkanes and alkenes) over CTA-POM catalyst in oil produced by thermal catalytic cracking. In contrast to ZSM-5, oil produced by thermal catalytic cracking over CTA-POM consists of C<sub>9</sub>-C<sub>13</sub> hydrocarbons with a maximum in the range of C<sub>9</sub>-C<sub>11</sub>. The percentage of paraffins was higher than olefins as discussed in Table 1.

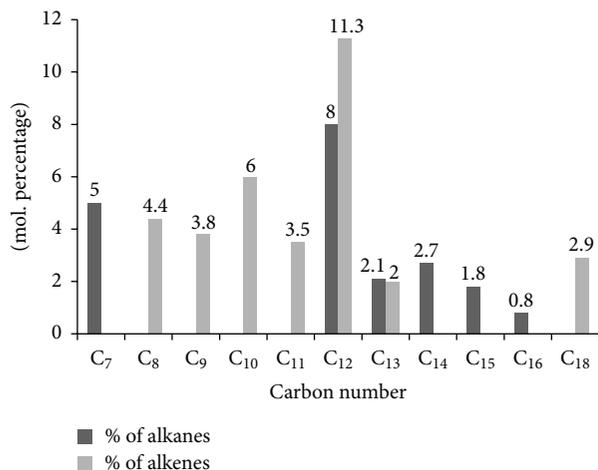


FIGURE 3: Distribution of alkanes and alkenes in oil produced by thermal catalytic cracking of LDPE over ZSM-5.

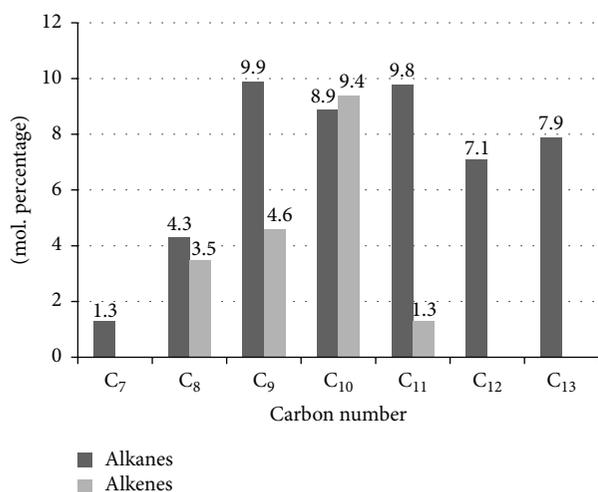


FIGURE 4: Distribution of alkanes and alkenes in oil produced by thermal catalytic cracking of LDPE over CTA-POM.

The thermal cracking of polyethylene over POM catalyst yields lower hydrocarbons which are more volatile as compared to ZSM-5.

**3.3. Mechanistic Consideration of Polymer Degradation over Catalysts.** According to Choomwattana et al. [18], ZSM-5 has confinement effect and shape selectivity due to the porous structure, while heteropoly acid (POM) possessed no confinement effect and such specific selectivity. However, POMs are more active in the protonation and activation of polymer cracking due to the presence of more protonic acidic sites than ZSM-5 which increases its catalytic efficiency many times. In CTA-POM, presence of organic group  $\text{CTA}^+$  induces hydrophobicity which increases its mobility in organic phase. It might lead to a better interaction with hydrocarbons and will result in improved selectivity and formation of more liquid component.

## 4. Conclusion

LDPE was degraded by thermal catalytic cracking using two different catalysts CTA-POM and compared with ZSM-5. The results showed that both catalysts degraded the polymer at very low temperature as compared to thermal degradation. GC-MS results showed that catalytic cracking of low density polyethylene beads generated more gasoline and diesel oil over CTA-POM as compared to ZSM-5. CTA-POM yields more useful oilier fraction as compared to ZSM-5. It is supposed that better activity of CTA-POM was due to hydrophobic nature of hexadecyl trimethyl ammonium part which helps in mobility of catalyst and increases its interaction with polymer.

## Competing Interests

The authors declare that they have no competing interests.

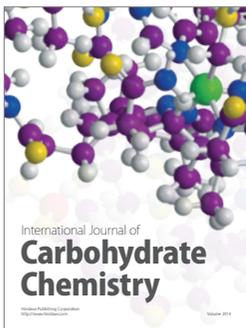
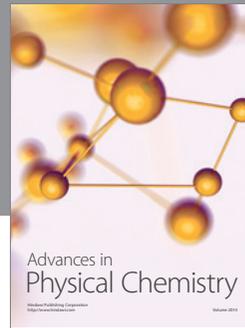
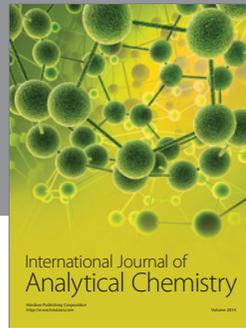
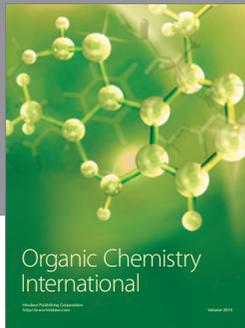
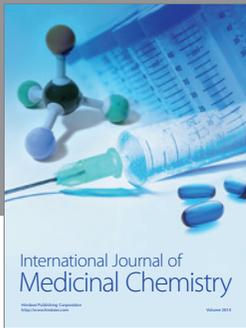
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