# PROMOTING EFFECT OF CO$_2$ ON THE DEGRADATION OF POLYETHYLENE TO ETHYLENE AND PROPYLENE OVER HZSM-5 CATALYST

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## Abstract

As a part of the recycling of waste plastics, degradation of polyethylene to ethylene and propylene with HZSM-5 catalyst was studied by using a two-step process (thermal cracking and catalytic cracking).

In the first stage, thermal cracking of high density polyethylene (HDPE) was carried out at 450-500 ℃. Yields of the cracked oil from HDPE were 79% at 450 ℃ and 88% at 500 ℃, respectively. Hydrocarbons of C7-C20 were the predominant products in the cracked oil. Higher hydrocarbons (>C20) increased with increasing reaction temperature.

In the second stage, in order to obtain lower alkenes (mainly C$_2$H$_4$ and C$_3$H$_6$), the catalytic cracking of the thermally-cracked oil obtained in the first stage was carried out using a HZSM-5 catalyst at 600 ℃ in N$_2$ and CO$_2$ atmospheres. Since the cracked oil was difficult to handle, $n$-C$_{16}$H$_{34}$, which was a representative product in the thermal cracking of HDPE, was employed as a model compound. HZSM-5 catalyst increased the C1-C4 gas yield to 50% and C$_2$H$_4$ + C$_3$H$_6$ yield to 12% in N$_2$ atmosphere. On the other hand, in CO$_2$ atmosphere the gas yield reached 61% and C$_2$H$_4$ + C$_3$H$_6$ yield reached 30%, respectively. Addition of CO$_2$ promoted the catalytic cracking of $n$-C$_{16}$H$_{34}$ with HZSM-5 to give C$_2$H$_4$ + C$_3$H$_6$.

## 1. Introduction

The amount of plastic waste is increasing all over the world [1-3]. Combustion and landfill are no longer acceptable for disposal of plastics because of serious environmental concerns and the low weight-volume ratio of plastics [1,4,5]. The recycling of waste plastics has received significant attention all over the world. Waste plastics can be recycled using three different methods: material recycling, thermal recycling, and chemical recycling. Material recycling is limited because of the high cost of sorting, the low quality of the recycled plastics, and the difficulty in finding a suitable market for recycled materials. Thermal recycling into fuel is the most promising method [6], with the recovered fuel used as an energy source. However, resources are finally combusted. Chemical recycling, which converts waste plastics into useful chemicals, has been recognized as the ultimate approach. Presently, about half of the waste is generated by factories in the form of specific plastics, such as polyolefins, polystyrene (PS), polyethylene terephthalate (PET), and polyvinylchloride (PVC). Several studies on the degradation of each of these types of waste plastic have been published.

PS can easily be decomposed into monomer by using a BaO catalyst[7]. PET can be degraded by hydrolysis under a steam atmosphere, yielding a quantitative amount of pure terephthalic acid and ethylene glycol as predicted from the chemical formula of PET[1].

Some of the polyolefins and vinyl polymers are very difficult to decompose into monomers because of random scission of the carbon-carbon bonds of the polymer chains[8,9]. Therefore, the thermal or catalytic degradation of polyolefin, especially polyethylene, into fuel has been examined by many scientists. The production of BTX by catalytic degradation of high density polyethylene (HDPE) has been reported[8]. On the other hand, the degradation of $n$-butane to ethylene and propylene by using mesoporous silica, mesoporous aluminosilicate, and zeolite was also reported[10-14]. However, studies to obtain ethylene and propylene from polyethylene have not so far been reported.

The objective of this work is to study the possibility of obtaining ethylene and propylene in the degradation of polyethylene with HZSM-5 catalyst by using a two-step process. The use of a two-stage reactor has two purposes: The first is the separation of impurities from the polluted waste plastics in the first-stage reactor. The second is the prevention of higher hydrocarbons contacting the catalyst layer in the second-stage reactor. The object of the first-stage reaction is to obtain low molecular weight hydrocarbons (with a carbon number of less than C20) by the thermal cracking of HDPE. The second-stage reaction is the catalytic conversion of the low molecular weight products to gases (mainly ethylene and propylene) with the catalyst. Moreover, since $CO_2$ promoted the oxidative dehydrogenation of alkanes[15] and ethylbenzene[16], we employed $CO_2$ in the catalytic cracking.

## 2. Experimental

### 2.1 Materials

High density polyethylene (HDPE) (specific gravity: 0.956 $g/cm^3$, melting point: 131 ℃) was obtained from Mitsui Chemicals Corporation, and was used in pellet form (3 x 3)mm. 1-Methylnaphthalene (1-MN), n-hexadecane ($n$-$C_{16}H_{34}$), and n-heptadecane ($n$-$C_{17}H_{36}$) were purchased from a commercial source.

HZSM-5 ($SiO_2/Al_2O_3$=22) was prepared according to the literature[17]. HY ($SiO_2/Al_2O_3$=200), Mordenite ($SiO_2/Al_2O_3$=20), and Ferrierite ($SiO_2/Al_2O_3$=20) were supplied from Tosoh Corporation.

### 2.2 Procedure

### 2.2.1 The first stage decomposition

The first stage reactor shown in Figure 1 was used for the cracking of HDPE. A 5.0 g of HDPE was charged into the reactor. The reactor was heated to the required temperature (450-550 ℃) and it was kept for 60 min in $N_2$ atmosphere. Gaseous products were separated from liquid at 0 ℃, and then collected in a gasbag after measuring the volume of gaseous products by using a gas burette. The degradation product was classified into three groups:
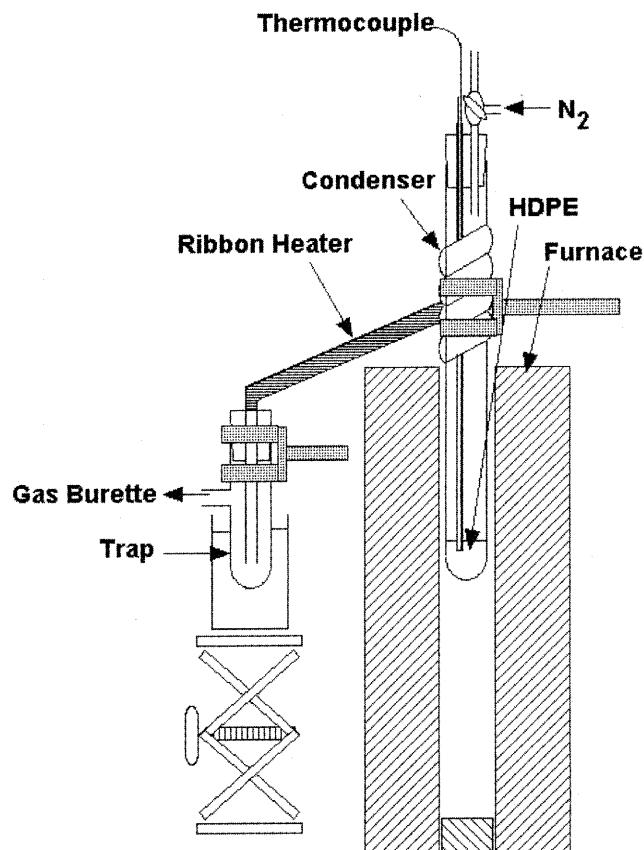
**Fig.1** Scheme of first stage reactor

gas (C1-C4), oil (C5 and higher hydrocarbons), and residue (remaining in the reactor).

## 2.2.2 The second stage decomposition

Figure 2 shows the fixed-bed type reactor used for the catalytic decomposition of $n$-$C_{16}H_{34}$. This reactor was heated at 20 °C/min to the required temperature (500-700 °C) and this was maintained for 120 min. Either $CO_2$ or $N_2$ was supplied as a carrier gas at a flow rate of 10 mL/min. $n$-$C_{16}H_{34}$ was fed (4 mL/h) into the reactor using a micro syringe pump. The degradation products from the reactor were separated into gas and oil fractions in a cold trap containing 1-MN maintained at 0 °C. As an internal standard, $n$-$C_{17}H_{36}$ was added to the oil fractions.

## 2.3 Product analyses

### 2.3.1 Gas chromatograph

Gaseous products were analyzed by a gas chromatograph (Shimadzu, GC-14B) equipped with an FID detector using a Porapack Q column (3.0 mm i.d × 3.1 m) for hydrocarbon (C1-C4), and a gas chromatograph (Shimadzu, GC-8A) equipped with a TCD detector using an activated carbon column (3.0 mm i.d. × 3.0 m) for hydrogen and CO. The liquid degradation

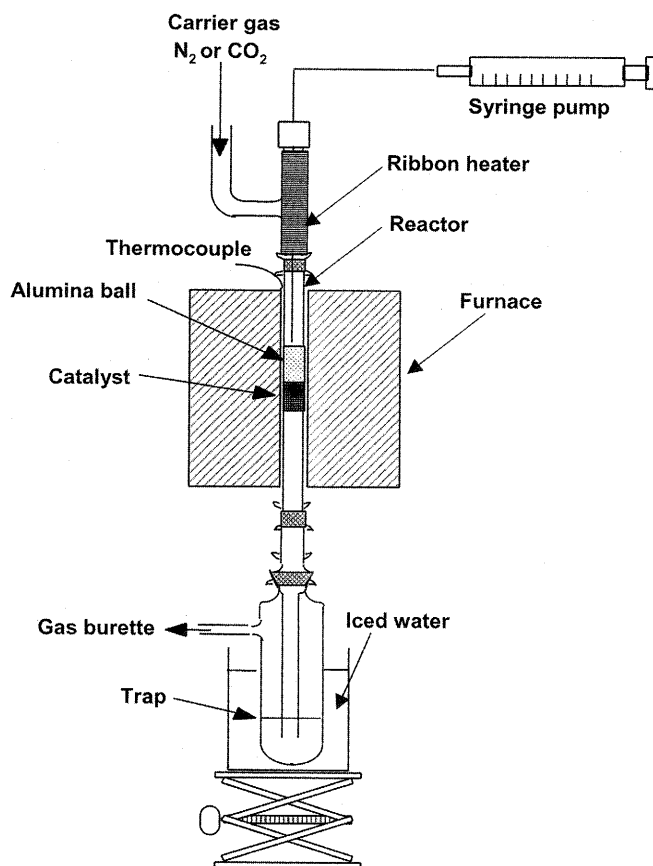**Fig.2**   Scheme of second stage reactor for $n\text{-}C_{16}H_{34}$

products of HDPE and $n\text{-}C_{16}H_{34}$ were analyzed by gas chromatograph (Shimadzu, GC-14A) equipped with a FID detector using a CBP1 capillary column (0.25 mm i.d. × 25m).

## 2.3.2 Thermogravimetric analysis

A thermogravimetric analyzer (TGA, Shimadzu, TG-50) was used to obtain the degradation temperature of HDPE and to evaluate the amount of carbon deposition on the catalytic surface. HDPE (or used HZSM-5) was loaded onto the TGA and then heated to 800 ℃ at 5-20 ℃/min in an air atmosphere (10 mL/min). The weight loss behavior was observed.

## 2.3.3 NH₃-TPD

The acidity and acid strength distribution of zeolite was performed with NH$_3$-TPD method using a BEL Japan, Inc. TPD-1-AT. The catalyst was heated to 500 ℃, maintained for 60 min, evacuated at 100 ℃, and then NH$_3$ was adsorbed at 100 ℃ with partial pressure of 20 Torr. The excess NH$_3$ was evacuated at 100 ℃ for 1h. Desorbed NH$_3$ was monitored with a quadrupole mass spectrometer. The amount of desorbed NH$_3$ was calibrated for the amount of NH$_3$ desorbed from a known solid acid.
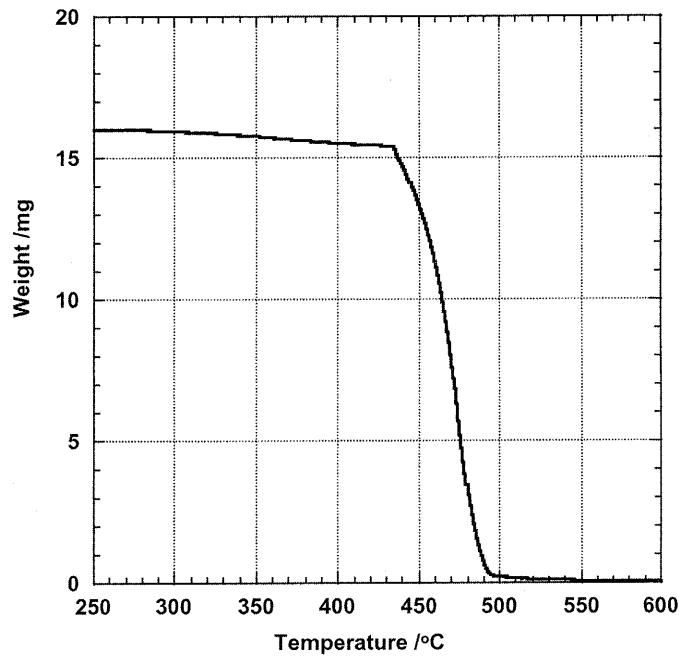
Fig.3   Weight loss curve of HDPE
Flow rate : $N_2$ = 10 mL/min
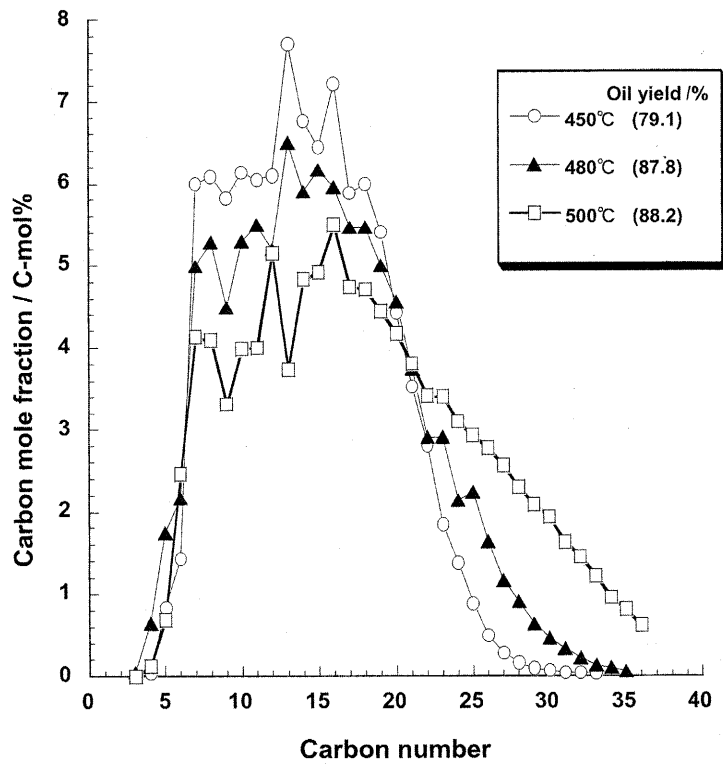Heating rate = 5 ℃/min



Fig.4   Effect of temperature on the carbon
number distribution of HDPE-cracked oil
HDPE : 5.0g   Reaction time : 3h

# 3. Results and Discussion

## 3.1 The first step decomposition (thermal cracking)

### 3.1.1 Effect of the reaction temperature on decomposition of HDPE

In order to obtain the optimal degradation temperature of HDPE, thermogravimetric analysis was carried out. The result is shown in Figure 3. HDPE was heated from a room temperature to 600 ℃ at a heating rate of 5 ℃/min under $N_2$ (10 mL/min). A gradual weight loss of HDPE began at 280 ℃, and rapidly decreased from 430 ℃ to 490 ℃. Therefore, the thermal cracking of HDPE was carried out at 450-500 ℃ in the first stage reactor.

The carbon number distributions obtained in the decomposition of HDPE at 450-500 ℃ are shown in Table 1 and Figure 4. The gas yield was very low (<3%), even at 500 ℃. The oil yield increased from 68% to 88% and the residue yield decreased from 28% to 4% with increasing reaction temperature from 450 ℃ to 500 ℃ (Table 1). Hydrocarbons of C7-C20 were the main products in the oil. The hydrocarbons of >C20 increased with increase in reaction temperature (Figure 4). The carbon number distribution should be shifted to that of lower molecular weight by adjusting the apparatus and the reaction conditions.

Table 1.   Dependence of product yield on the reaction temperature of thermal cracking of HDPE

| Run | Temp. (℃) | Yield (wt%) | | | | Mole (mmol/g-HDPE) | | | | | | | |
|-----|-----------|-----|-----|---------|------|------|------|------|------|------|------|------|------|
|     |           | Gas | Oil | Residue | M.B. | C1 | C2= | C2 | C3= | C3 | C4= | C4 | $H_2$ |
| 1 | 450 | 2.1 | 67.6 | 28.1 | 97.9 | 0.15 | 0.14 | 0.17 | 0.15 | 0.11 | 0.06 | 0.05 | 0.07 |
| 2 | 480 | 2.7 | 87.9 | 4.7 | 95.9 | 0.15 | 0.15 | 0.16 | 0.15 | 0.11 | 0.05 | 0.03 | 0.02 |
| 3 | 500 | 3.4 | 88.2 | 3.5 | 95.4 | 0.19 | 0.22 | 0.20 | 0.22 | 0.15 | 0.07 | 0.05 | 0.03 |

HDPE : 5.0g, Reaction time : 3 h, $N_2$ atmosphere

## 3.1.2 Effect of residence time on the carbon number distribution of the oil

In order to increase the residence time of the reactant in the reactor, the upper part of the reactor was cooled with a water jacket. The carbon number distribution of the oil obtained in the decomposition of HDPE with this reactor is shown in Figure 5. The carbon numbers of the main product from this run decreased from C18 to C8, when HDPE was decomposed at a reaction temperature of 480 ℃ using the water-cooled reactor. However, the oil yield decreased from 88% to 64% and the residue yield increased from 4% to 18%. Hydrocarbons of >C20 are the main products in the residue after decomposition of HDPE at 480 ℃ using the water-cooled reactor. The residue must be decomposed into lower hydrocarbons by repeated heating.

In order to avoid vaporization of higher hydrocarbons (> C20), decomposition of the residue was carried out by a temperature-programmed reaction. This temperature program was as follows. Firstly, from room temperature to 380 ℃ at a heating rate of 20 ℃/min in $N_2$ atmosphere; the second step heating was at a heating rate of 5 ℃/min maintained for 20 min at 480 ℃; and the third step was heating the residue to 520 ℃ at 5 ℃/min and maintaining it for 20 min. The results are shown in Figure 6. As a result of staged heating,
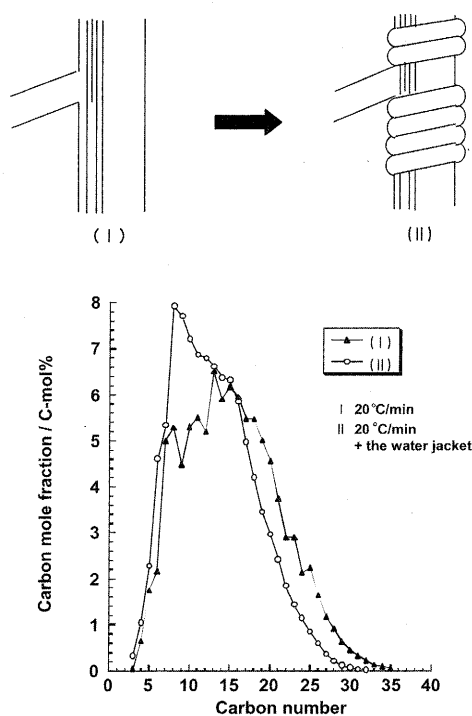
**Fig.5** Effect of partial condenser on the carbon number distribution of HDPE-cracked oil
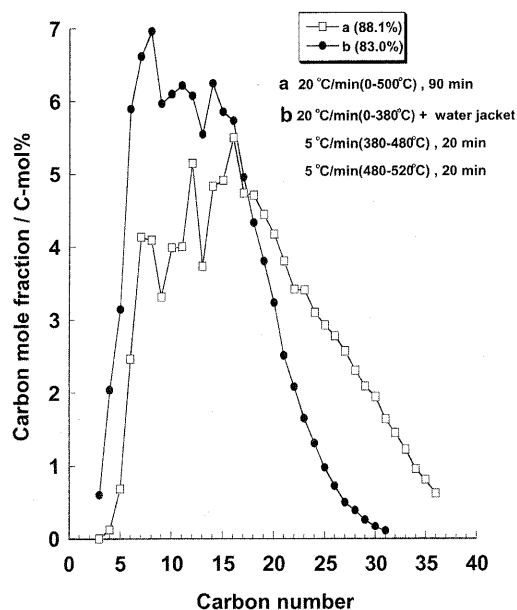HDPE : 5.0g   Reaction temperature : 480℃

**Fig.6** Carbon number distribution of HDPE-cracked oil in a temperature-programmed reaction

the oil yield increased from 64 to 83% and the carbon number distribution shifted to the lower molecular weight side as compared to the degradation of HDPE using a constant heating rate without the water jacket. By controlling the heating pattern and applying water cooling to the top of the reactor, the lower molecular weight fraction in the oil increased.

## 3.2 The second step (catalytic cracking)

### 3.2.1 Decomposition of $n$-$C_{16}H_{34}$ with various catalysts

Since it is difficult to handle the oil from the first stage due to its high melting-point, $n$-$C_{16}H_{34}$ was used as a model compound in the second step reaction instead of the oil product from HDPE. Table 2 (Runs 4-6) shows the yield of products obtained in the thermal

**Table 2.** Product yields in the degradation of $n$-$C_{16}H_{34}$ without catalyst

| Run | Temp. (℃) | Conversion (%) | Yield (wt%) | | | Mole (mmol/g-$C_{16}H_{34}$) | | | | | | | |
|-----|-----------|----------------|------|------|------|------|------|------|------|------|------|------|------|
| | | | Gas | Oil | Coke | C1 | C2= | C2 | C3= | C3 | C4= | C4 | H2 |
| 4 | 500 | 11.0 | 1.2 | 93.1 | 0.6 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 |
| 5 | 600 | 39.9 | 15.9 | 78.9 | 0.2 | 0.28 | 0.50 | 0.21 | 0.21 | 0.01 | 0.03 | 0.00 | 0.03 |
| 6 | 700 | 96.9 | 50.7 | 28.8 | 0.5 | 1.04 | 2.03 | 0.41 | 0.54 | 0.01 | 0.09 | 0.01 | 0.23 |

$n$-$C_{16}H_{34}$ : 4 mL/min, $N_2$ : 10 mL/min, Reaction time : 0.5 h

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degradation of $n$-$C_{16}H_{34}$ at 500-700℃ without catalyst. The oil yield decreased from 93% to 28% and the gas yield increased from 1.2% to 51% by increasing the cracking temperature from 500 ℃ to 700 ℃. The principal reaction seems to be a thermal cracking at 700 ℃. Therefore, the catalytic cracking of $n$-$C_{16}H_{34}$ was performed at 600 ℃.

The effect of various zeolites, such as HY, HZSM-5, Mordenite and Ferrierite on the catalytic cracking of $n$-$C_{16}H_{34}$ under $N_2$ (10 mL/min) was examined, and the results are shown in Figure 7. The gas yields with HY, Mordenite and Ferrierite as a catalyst were smaller than those of the thermal degradation at the same temperature. We conclude that HY, Mordenite and Ferrierite did not act as catalysts under these conditions. On the other hand, in the catalytic cracking of $n$-$C_{16}H_{34}$ with HZSM-5 ($SiO_2/Al_2O_3$=22), the gas yield increased from 16% to 50% as compared to the thermal cracking of $n$-$C_{16}H_{34}$, and the $C_2H_4$ + $C_3H_6$ yield reached 12%. HZSM-5 ($SiO_2/Al_2O_3$=22) was the most effective of the catalysts employed here.
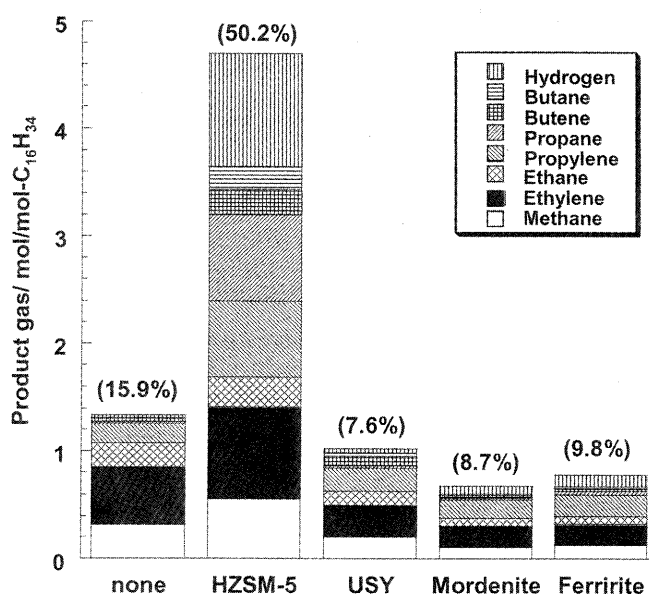


Fig.7  Effect of catalysts on gas yield in the degradation of $n$-$C_{16}H_{34}$
$n$-$C_{16}H_{34}$ : 4 mL/h  Reaction time : 2h  $N_2$ : 10 mL/h  W/F : 7.53 g-cat·h/mol
Reaction temperature : 600℃  ( ) : gas yield

## 3.2.2 Effect of $CO_2$ addition on the degradation with HZSM-5

In order to increase olefin yield, the use of $CO_2$ as a promoter of dehydrogenation of hydrocarbons was examined. The effect of $CO_2$ addition on the degradation with HZSM-5 ($SiO_2/Al_2O_3$=22) is shown in Table 3 (Runs 7 and 8). Under $CO_2$ the gas yield and the $C_2H_4$ + $C_3H_6$ yield increased to 61% and 30%, respectively, as compared with the reaction under $N_2$. The $CH_4$ yield decreased from 0.67 to 0.14 mol/mol-$C_{16}$ and the $C_3H_6$ yield increased from 0.49

**Table 3.** Product yields in the degradation of $n$-$C_{16}H_{34}$ with various zeolites

| Run | Temp. (℃) | Conversion (%) | Yield (wt%) | | | Mole (mmol/g-$C_{16}H_{34}$) | | | | | | | |
|-----|-----------|----------------|------|------|------|------|------|------|------|------|------|------|------|
| | | | Gas | Oil | Coke | C1 | C2= | C2 | C3= | C3 | C4= | C4 | H2 |
| 4 | 500 | 11.0 | 1.2 | 93.1 | 0.6 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 |
| 5 | 600 | 39.9 | 15.9 | 78.9 | 0.2 | 0.28 | 0.50 | 0.21 | 0.21 | 0.01 | 0.03 | 0.00 | 0.03 |
| 6 | 700 | 96.9 | 50.7 | 28.8 | 0.5 | 1.04 | 2.03 | 0.41 | 0.54 | 0.01 | 0.09 | 0.01 | 0.23 |

$n$-$C_{16}H_{34}$ : 4mL/min, Catalyst : 0.1 g, $N_2$ : 10mL/min, Reaction temperature : 600℃ Reaction time : 2 h

to 0.85 mol/mol-$C_{16}$. The amount of aromatic compounds (BTX) in the decomposed oil under $CO_2$ decreased sharply from 26% to 8% as compared to the reaction under $N_2$. From these results, we can see that $CO_2$ seems to affect not only the dehydrogenation of alkane to alkene but also the aromatization of alkene, because $CO_2$ prevents re-adsorption of $C_3H_6$ on the HZSM-5 surface[18].

The acidity and the acid strength distribution of HZSM-5 ($SiO_2/Al_2O_3$=22) before and after the decomposition of $n$-$C_{16}H_{34}$ in $CO_2$ and $N_2$ atmospheres were analyzed by using $NH_3$-TPD. The acid strength distribution of HZSM-5 hardly changed before and after the reaction. However, in $CO_2$ atmosphere the acidity of HZSM-5 after the degradation of $n$-$C_{16}H_{34}$ decreased from 0.8 to 0.08 mmol/g as compared to that before the reaction. This result clearly indicates that addition of $CO_2$ greatly changed the acidic property of the HZSM-5 surface during the catalytic cracking of $n$-$C_{16}H_{34}$. Consequently, the amount of BTX in the oil fraction decreased in relation to the amount of catalytic cracking under $N_2$.

## 4. Conclusion

By controlling the heating pattern and applying water cooling to the top of the first stage reactor, the oil yield from HDPE increased from 64% to 83% and the carbon number distribution shifted to the lower molecular weight side as compared to the degradation of HDPE using one-step heating without the water jacket.

The promoting effect of $CO_2$ on catalytic cracking over HZSM-5 ($SiO_2/Al_2O_3$=22) was recognized. By means of adding $CO_2$ into the degradation with HZSM-5 ($SiO_2/Al_2O_3$=22), the obtained gas, especially the amount of $C_2H_4+C_3H_6$, increased whereas the amount of aromatic compounds (BTX) decreased as compared to catalytic cracking under $N_2$. $CO_2$ seems to affect not only the dehydrogenation of alkane to alkene but also the aromatization of alkene

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