



# 폐플라스틱의 촉매 열분해 Review

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# 폐기물 열분해기술의 필요성

## ❖ 폐기물의 환경친화적인 처리 (소각 대체 기술)

- 2차 폐기물의 발생 가능성 낮음
- 대기오염 배출물질의 가능성 낮음

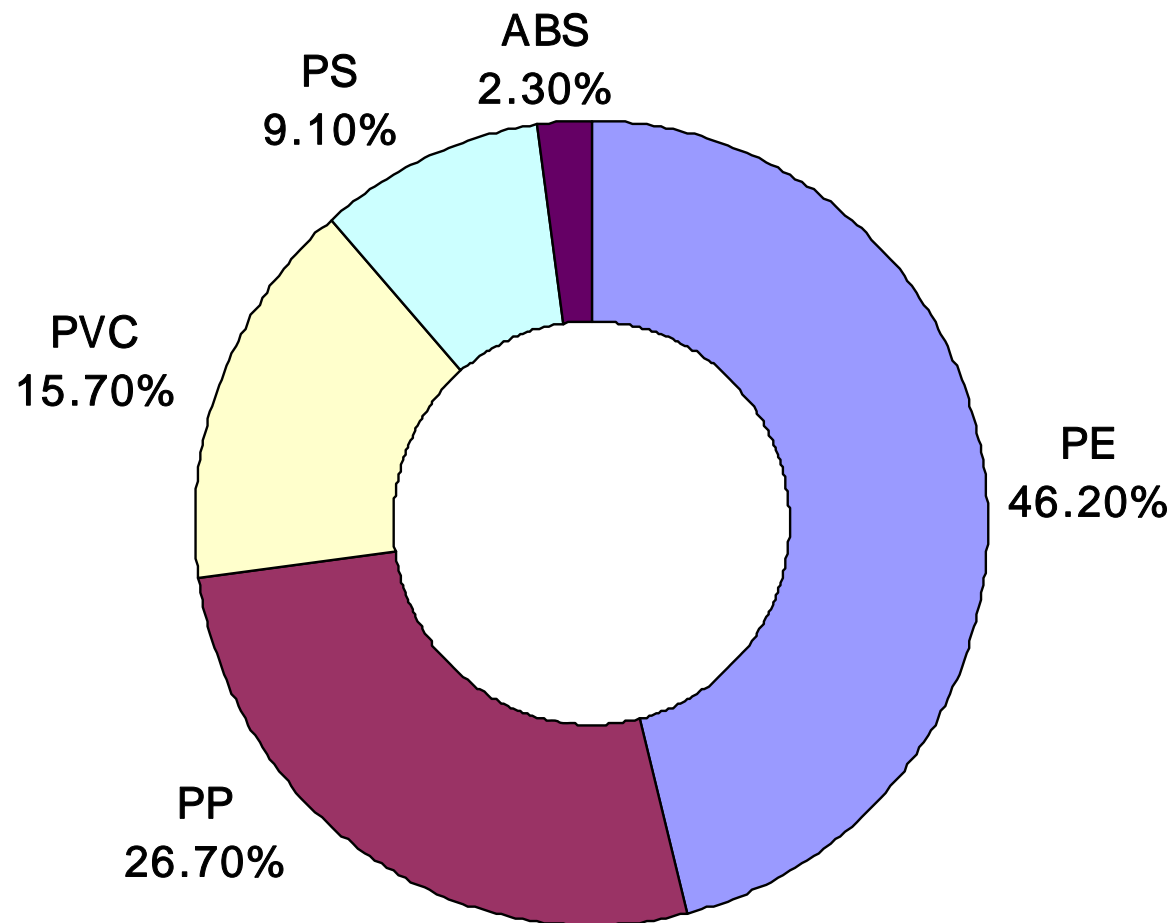
## ❖ 열분해 생성물의 활용 가치 및 효율이 높음

- 재생유의 경유 대체연료로 사용가능
- 저장 및 이동 등 효용성이 높음

## ❖ 고분자 폐기물의 대체 에너지화 자원 활용

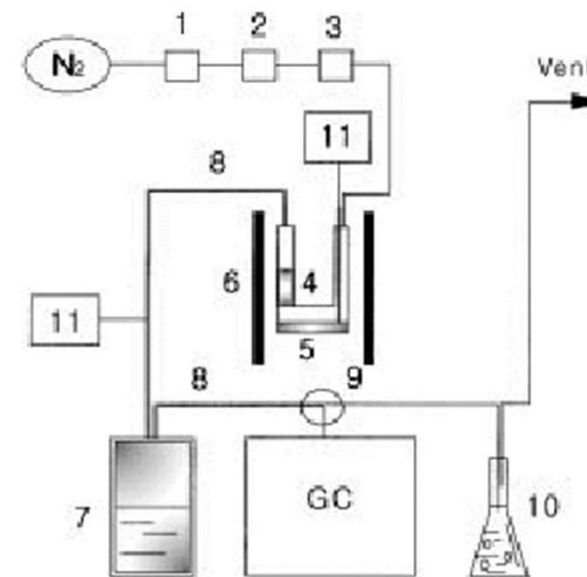
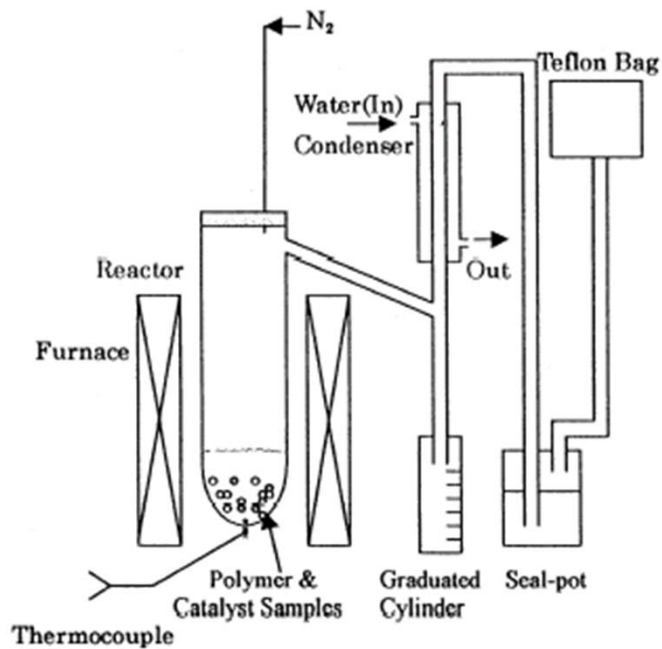
- 에너지 수입 대체효과 극대화
- 폐기물의 효율적인 이용 및 환경오염 문제 처리

# 국내 폐플라스틱 성분별 발생분포

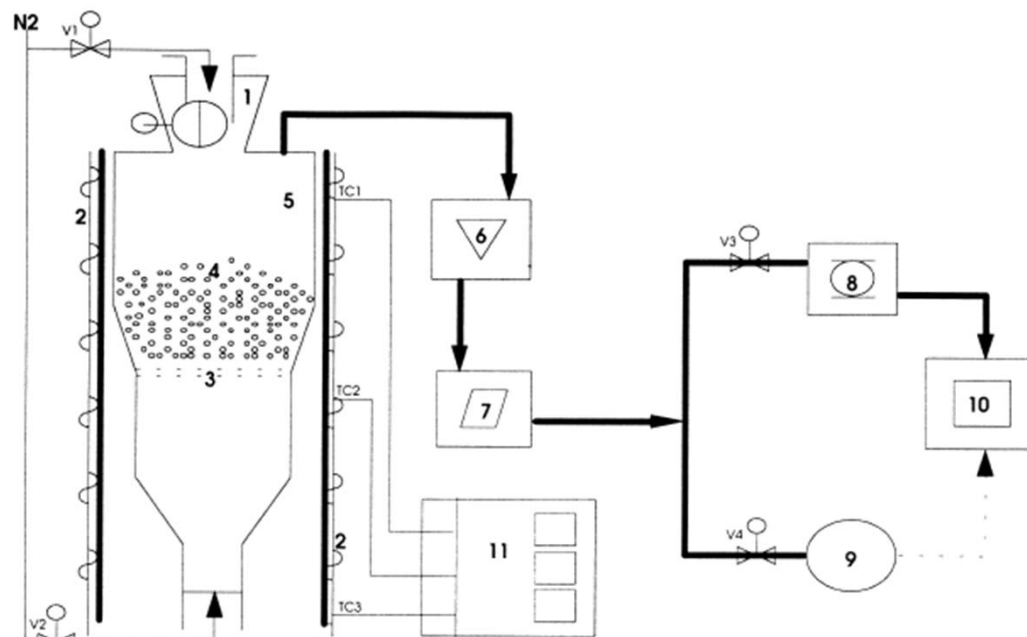
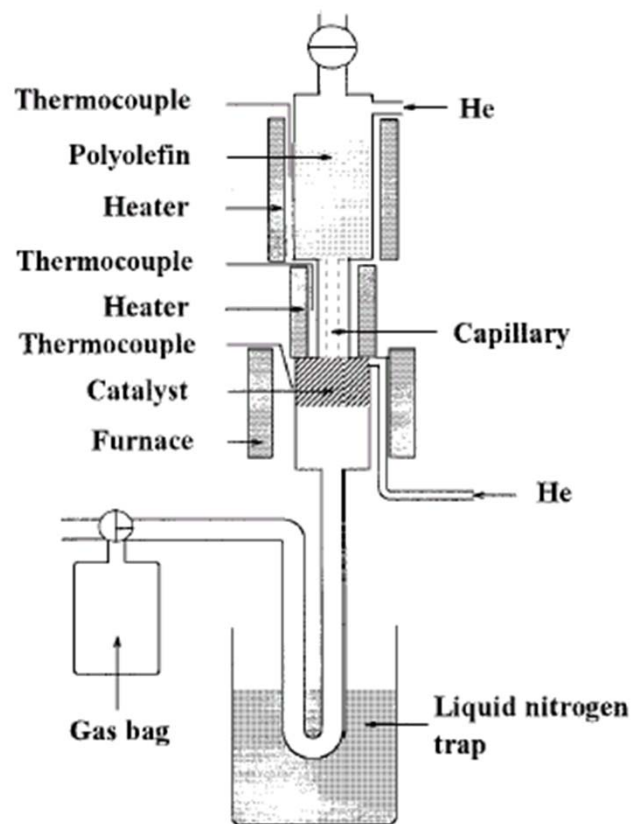


\* Ref : 한국자원재생공사 (2000)

# 반응기 형태 (회분식, 반회분식)



# 반응기 형태 (고정층, 유동층)



# 반응 접촉 형태 (액상, 기상)

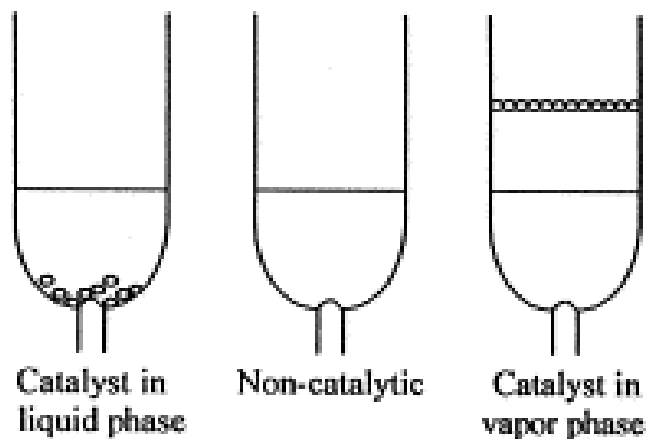
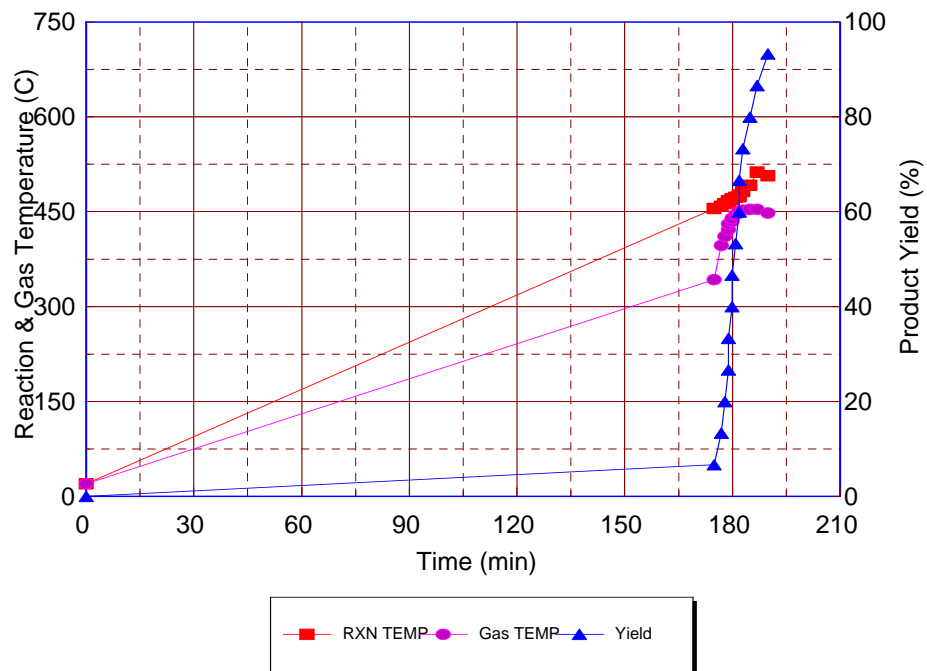


Table Product yield (wt%) for thermal and catalytic degradation of PP at 380°C [Ref. 61]

Contact phase of catalysts	Non-catalytic (thermal)	Silica-alumina (vapor phase)	Silica-alumina (liquid phase)
Product yield			
Liquid	64.9	54.5	68.8
Gaseous	24.7	35.0	24.8
Residues	10.4	10.5	6.4

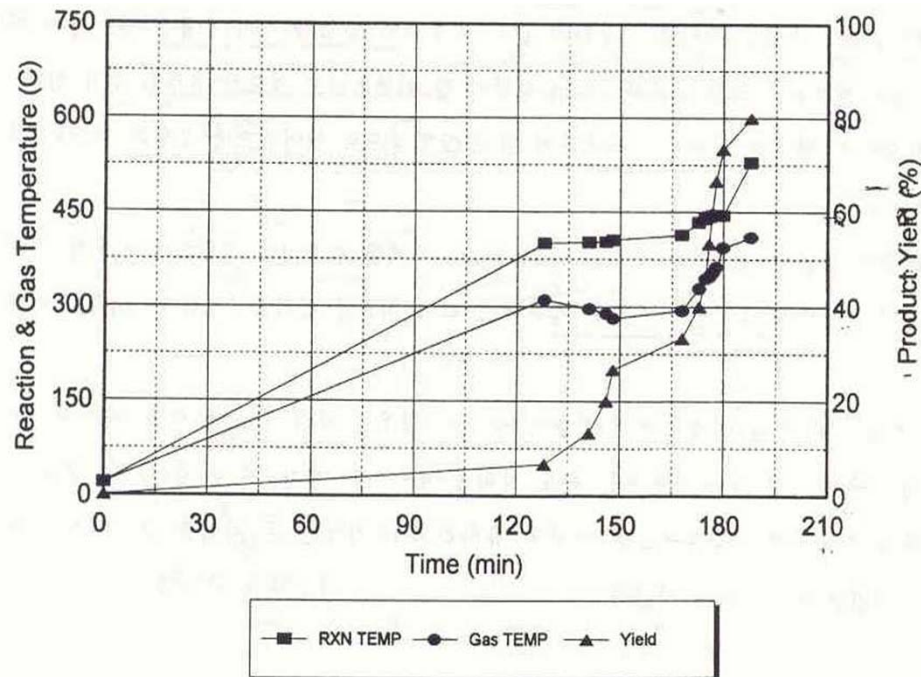
# LDPE 열분해

## 촉매 불사용



- ❖ 열분해 개시온도 : 450°C
- ❖ 최종분해 온도 : 500 °C
- ❖ 생성물 : wax 형태

## Mordenite 촉매 사용



- ❖ 열분해 개시온도 : 380°C
- ❖ 최종분해 온도 : 500 °C
- ❖ 생성물 : oil 형태
- ❖ 촉매사용시 동일 수율에서 분해온도 감소

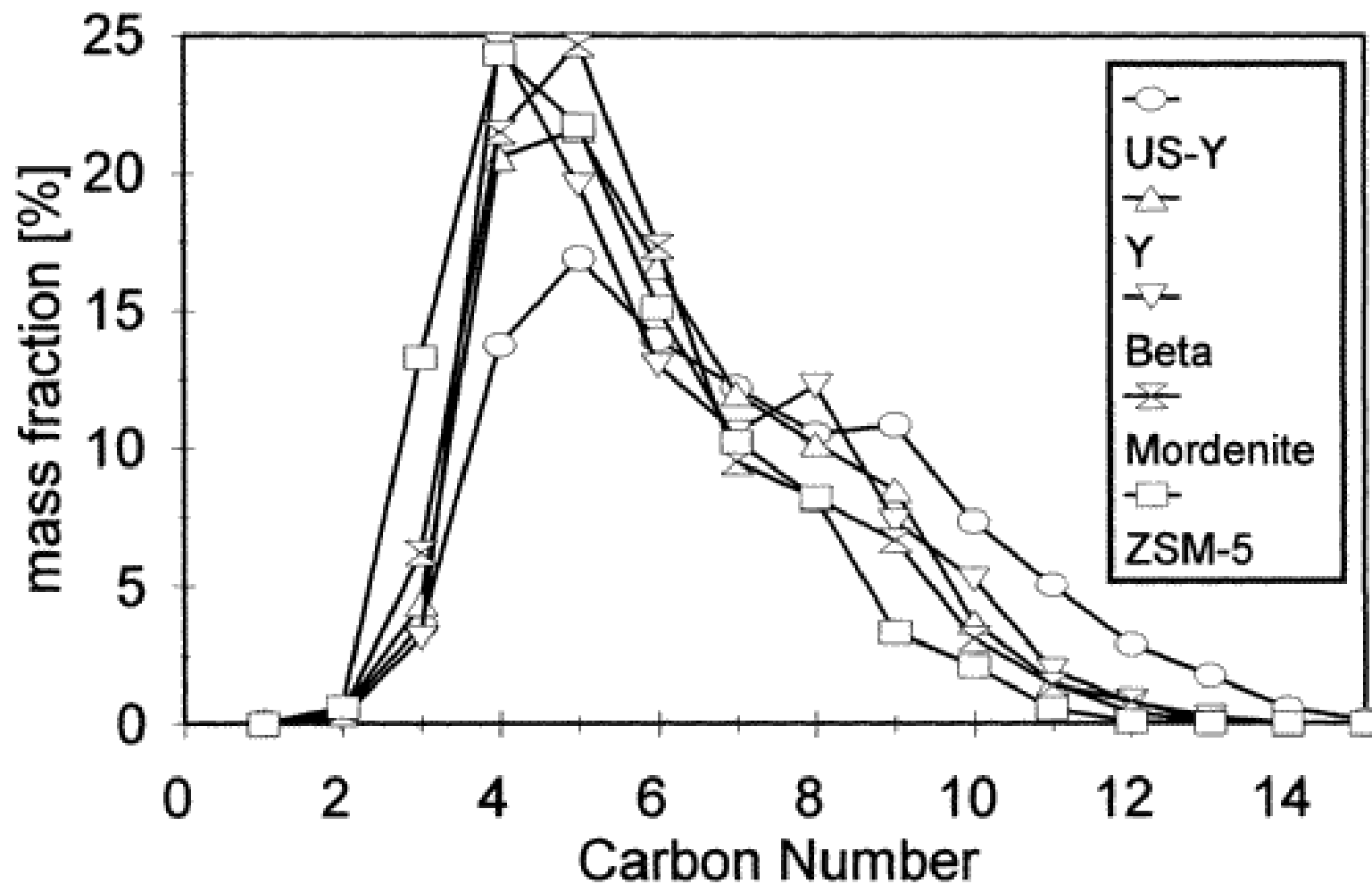
# 촉매 사용시 활성화에너지

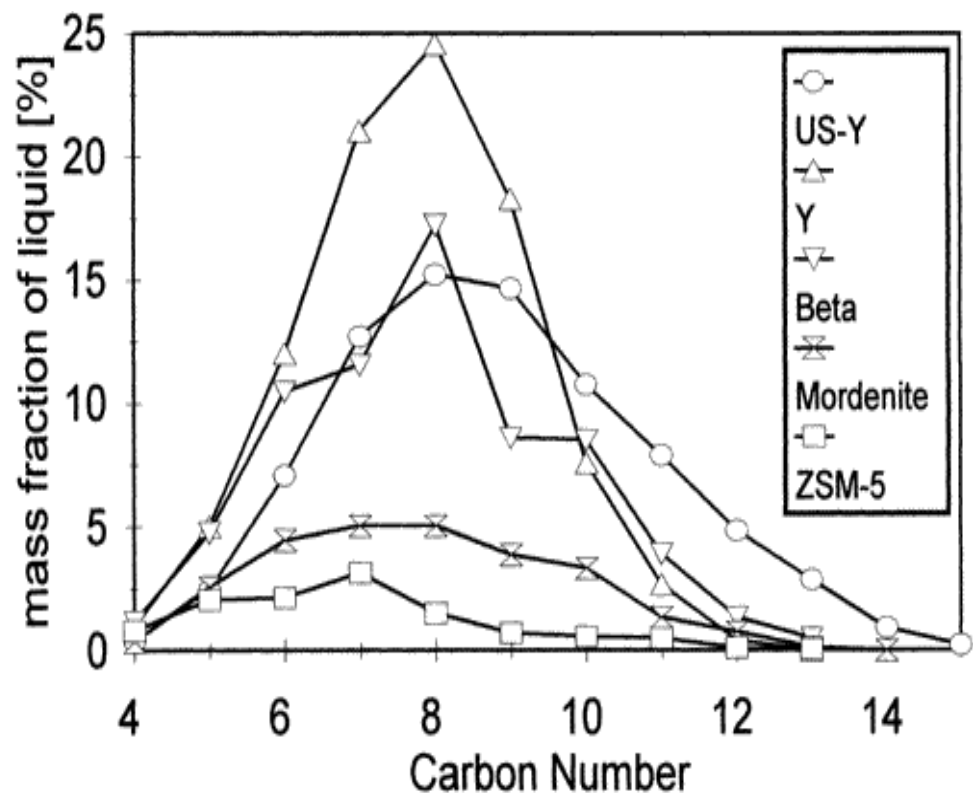
Table Effects of catalysts on the activation energy  $E_a$  for cracking of polyolefinic plastics [Ref. 78]

Catalyst	$E_a$ (kJ/mol) by Ozawa model
HZSM-5 (17)	118
HZSM-5 (70)	114
HY	119
HUSY	118
MCM-41 (Al)	74
MCM-41 (Si)	209
Silica-Alumina	128
No catalyst	255

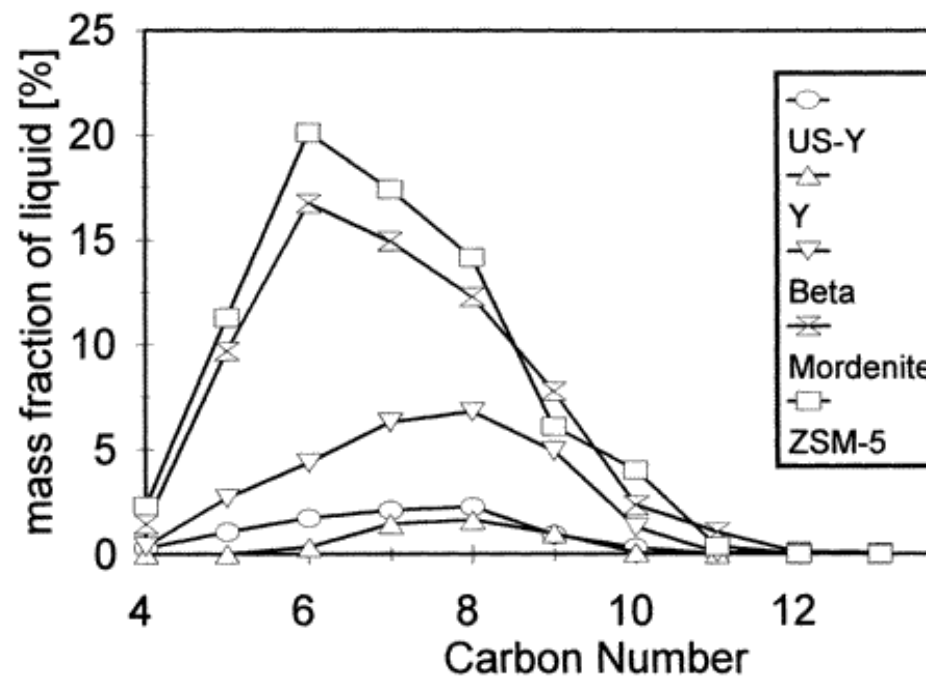


## 기공 크기의 영향, Dwyer et al.





Liquid alkane distribution



Liquid alkene distribution

## 세공구조(세공 모양) 영향, Seo et al. (HDPE 분해)

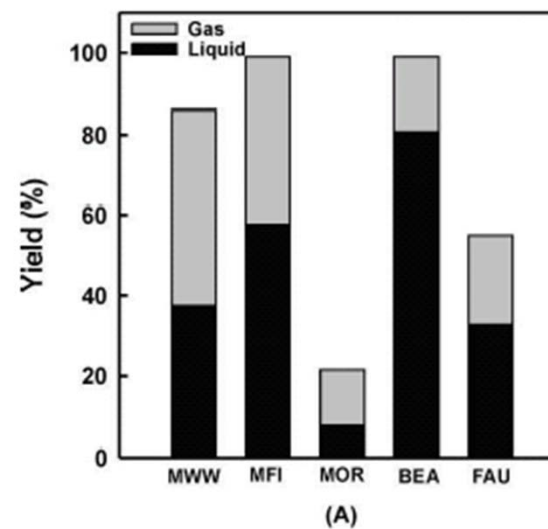
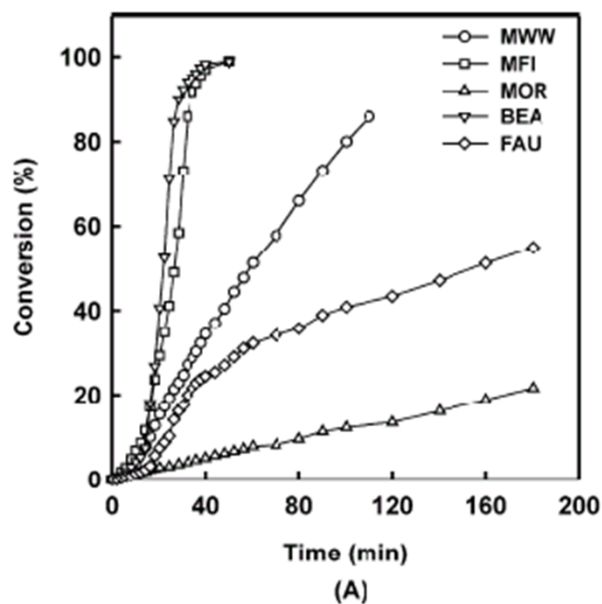


Fig. 7. Liquid-phase degradation of HDPE over

# Degradation of PE and PP into fuel oil by using solid acid and non-acid catalyst (Sakata et. al.) (1)

## Acid-catalysts

- ① silica alumina SA-1, SA-2
- ② zeolite ZSM-5

## Non acidic mesoporous silica catalysts

- ① silicalite
- ② amorphous mesoporous silica gel (Q3)
- ③ crystalline mesoporous folded silica (FSM)

→ uniform hexagonal pores (2.7 nm)

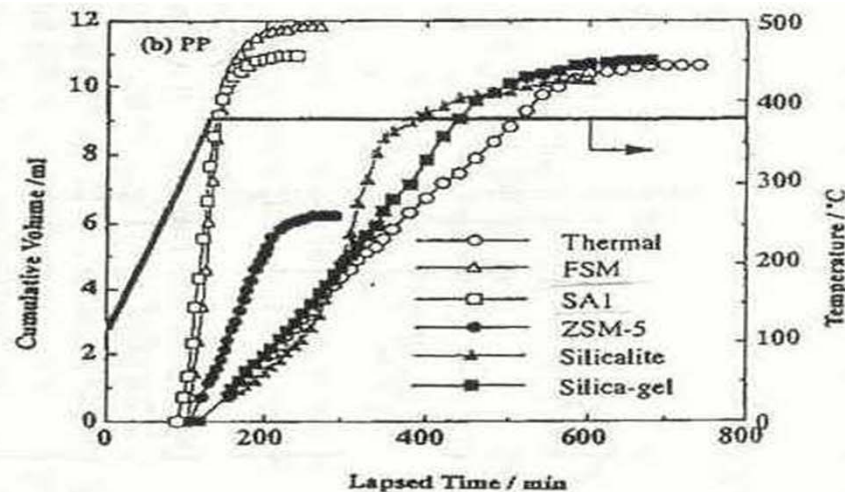
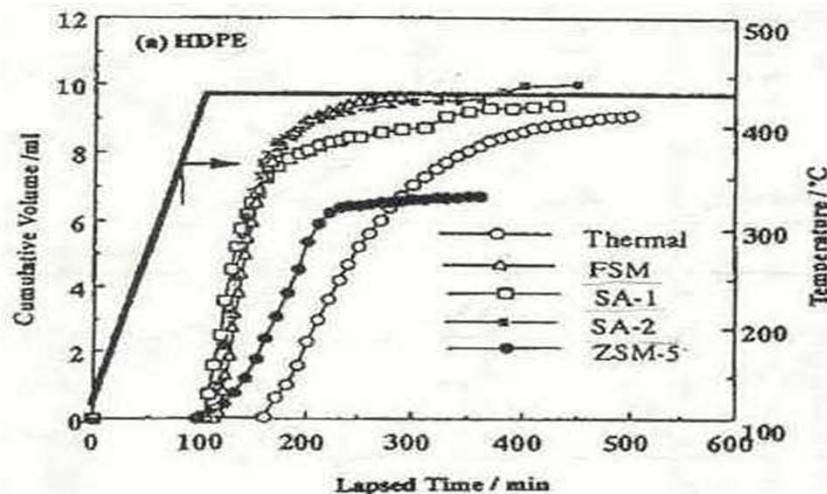


Fig. Cumulative vol. of liquid products from thermal and catalytic degradation of (a) HDPE at 430 °C and (b) PP at 380°C

## Degradation of PE and PP into fuel oil by using solid acid and non-acid catalyst - (2)

- ❖ SA-1, ZSM-5, FSM : n-C5 ~ n-C15 (36 ~ 270°C)
  - ➔ thermal degradation과 비교해볼 때 FSM은 폴리머의 분해속도 뿐만 아니라 heavier waxy 성분을 lighter 액체 탄화수소로 분해하도록 촉진시킴.
- ❖ silicalite & silica-gel : thermal degradation과 유사한 액체 생성물 생성됨.

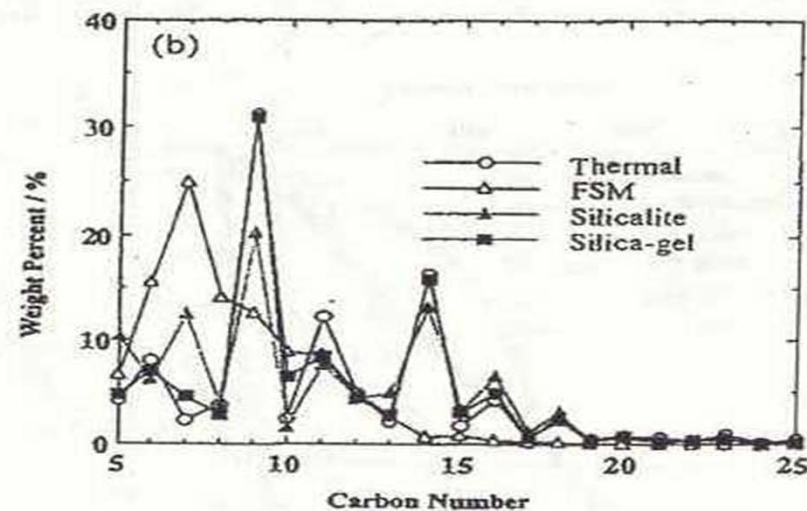
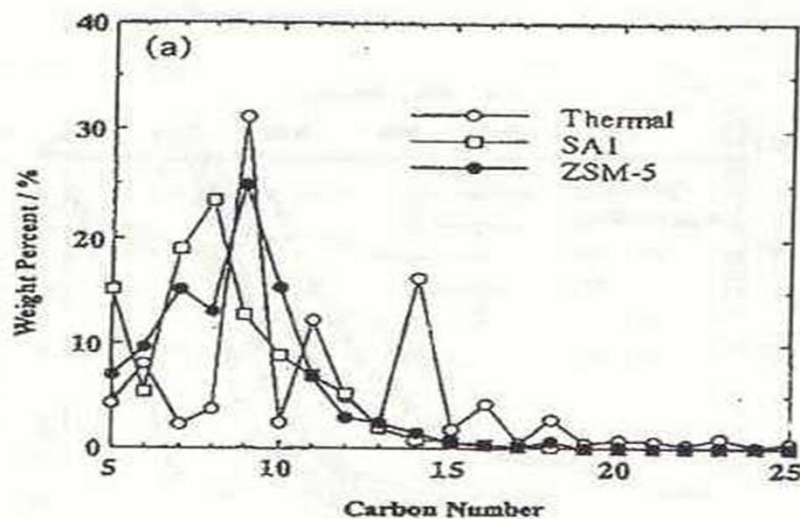
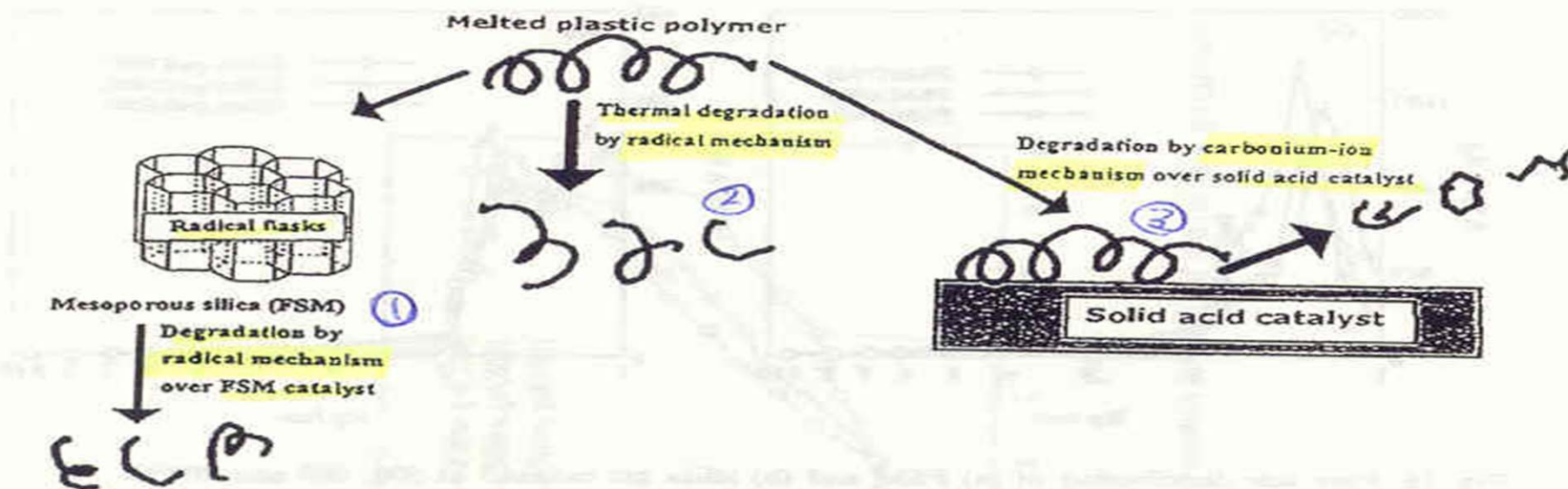


Fig. Carbon number distribution (NP-gram) of liquid products from thermal and catalytic degradation of PP at 380°C

## Degradation of PE and PP into fuel oil by using solid acid and non-acid catalyst - (3)

### Mechanism of polymer degradation over a FSM catalyst by Sakata et al



### ‘Radical flask’

- ❖ FSM 촉매는 acid site를 가지고 있지는 않지만 PE와 PP의 분해를 상당히 증진시킴.
- ❖ FSM에 의한 polyolefins의 분해 메카니즘은 촉매의 acid sites가 아닌 촉매의 hexagonal large pore 구조와 같은 독특한 특징에 의해 크게 영향받음.

## Pure silica form – MCM-41 (5.1 nm),

Table Composition of gaseous product [Ref. 4]

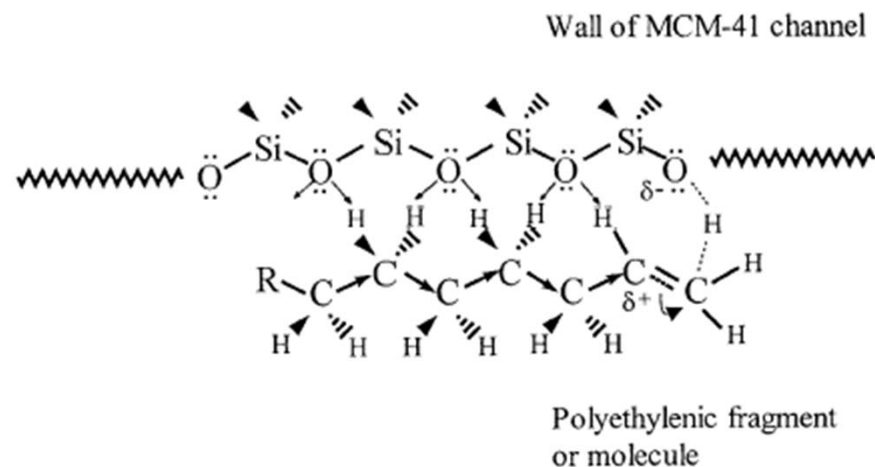
Catalyst	Temp. (°C)	Gaseous product composition (wt%)							(iC4P)/	(iC4=)/
		C1	C2	C2=	C3	C3=	C4	C4=	(nC4P)	(ΣC4=)
MCM-41(1) <sup>a</sup>	450	0.16	0.5	0.23	0.78	2.49	0.80	3.62	0.95	0.51
MCM-41(2) <sup>p</sup>	450	0.29	1.09	0.50	1.60	1.51	0.99	1.49	0.00	0.07
MCM-41(3) <sup>p</sup>	450	0.12	0.34	0.19	0.65	2.07	0.78	3.58	1.00	0.45
MCM-41(3) <sup>p</sup>	410	0.04	0.11	0.08	0.30	2.15	0.72	3.60	5.31	0.49
MCM-41(3) <sup>p</sup>	430	0.02	0.06	0.04	0.22	1.58	0.82	2.97	3.50	0.50
None	410	0.40	1.11	0.28	1.34	1.33	0.81	0.95	0.04	0.11
None	430	0.44	1.29	0.44	1.75	1.94	1.01	1.26	0.01	0.10
None	450	0.11	0.71	0.25	1.34	1.43	0.83	1.06	0.00	0.09

<sup>a</sup> Synthesized by conventional method,

<sup>b</sup> Synthesized by microwave, degree of crystallinity is 75% of that of MCM-41(3)

# Degradation of PE fuel oil by using pure silica MCM-41 (5.2 nm) Seddegi et al

## Mechanism of polymer degradation over a MCM-41 by Seddegi et al



**이소부텐과 이소부탄(iC4/nC4=5.3)을 반응생성물로 얻음 - 산점에서**

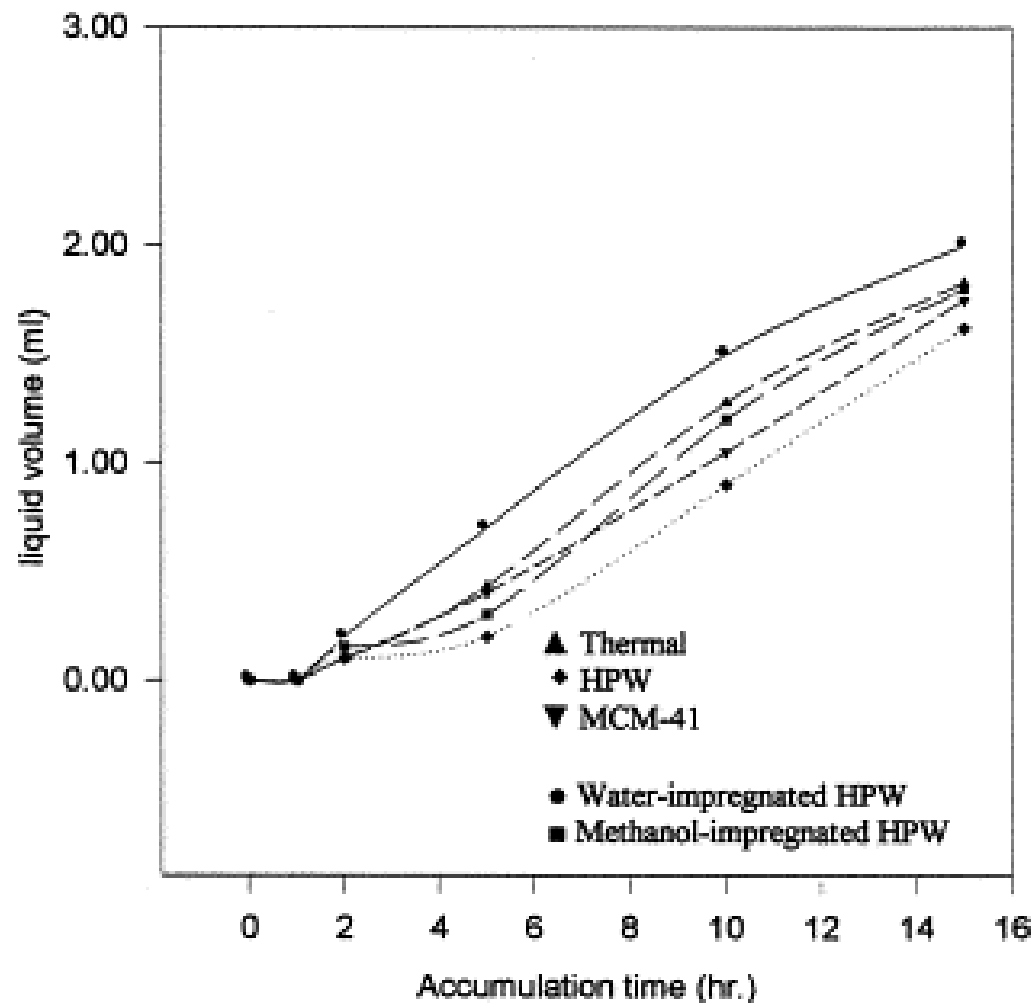
**일어나는 반응특성**

❖ Channel 내의 silanol group이 산점의 역할

❖ 가교 산소 원자와 PE 분자의 수소 원자들간들의 상호 작용으로 인해 카르베니움 이온이 안정하게 생성되고 결국은 산촉매에서와 같은 반응이 일어난다고 제안



## Pure silica form – MCM-41 (4.8 nm), Jalil et al.



- 열분해보다 활성이 저조
- 기공크기가 작은 경우엔 활성이 열분해보다 우수

# 촉매 사용시 활성화에너지 (기공크기 확인)

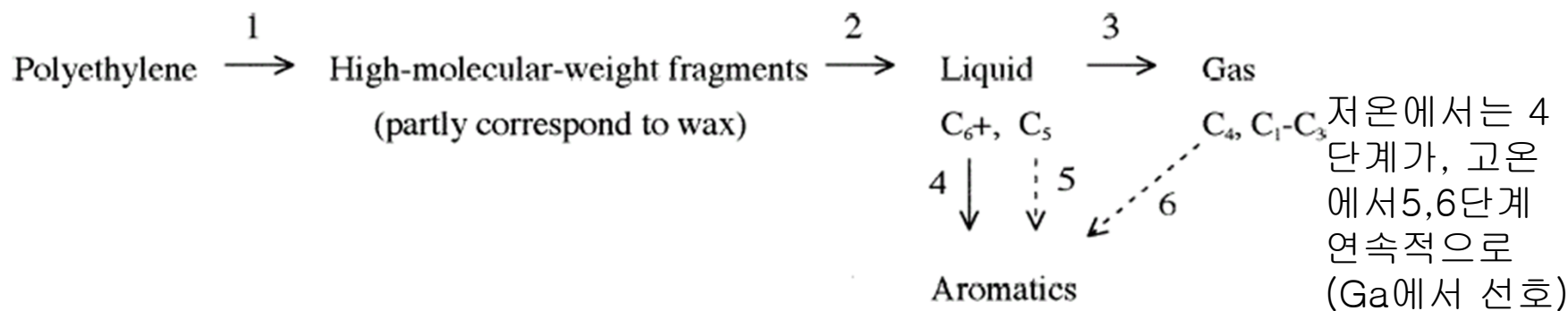
Table Effects of catalysts on the activation energy  $E_a$  for cracking of polyolefinic plastics [Ref. 78]

Catalyst	$E_a$ (kJ/mol) by Ozawa model
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HZSM-5 (70)	114
HY	119
HUSY	118
MCM-41 (Al)	74
MCM-41 (Si)	209
Silica-Alumina	128
No catalyst	255

## H-Ga-silicate (방향족 생성이 탁월) – Uemichi et al.

Table Yields of products from thermal and catalytic degradation of polyethylene [Ref. 63]

	Thermal	H-Ga-silicate	H-Ga-silicate	HZSM-5	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
온도 (°C)	525	400	525	525	525
Yield (wt,%)					
Gas	7.6	40.3	28.0	58.0	57.2
Liquid	13.1	59.4	72.0	42.0	42.1
Aromatics	- <sup>a</sup>	44.1	71.6	40.8	9.5
BTX	- <sup>a</sup>	30.1	61.8	33.5	3.7
Wax	79.2	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
Coke	0.1	0.3	- <sup>a</sup>	- <sup>a</sup>	0.4



Scheme 1.

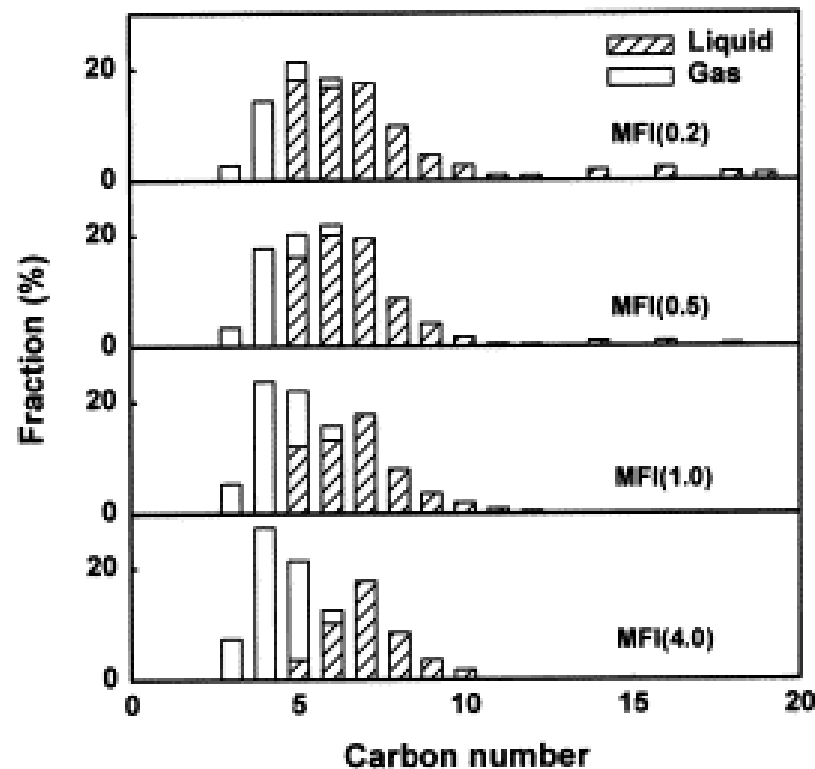
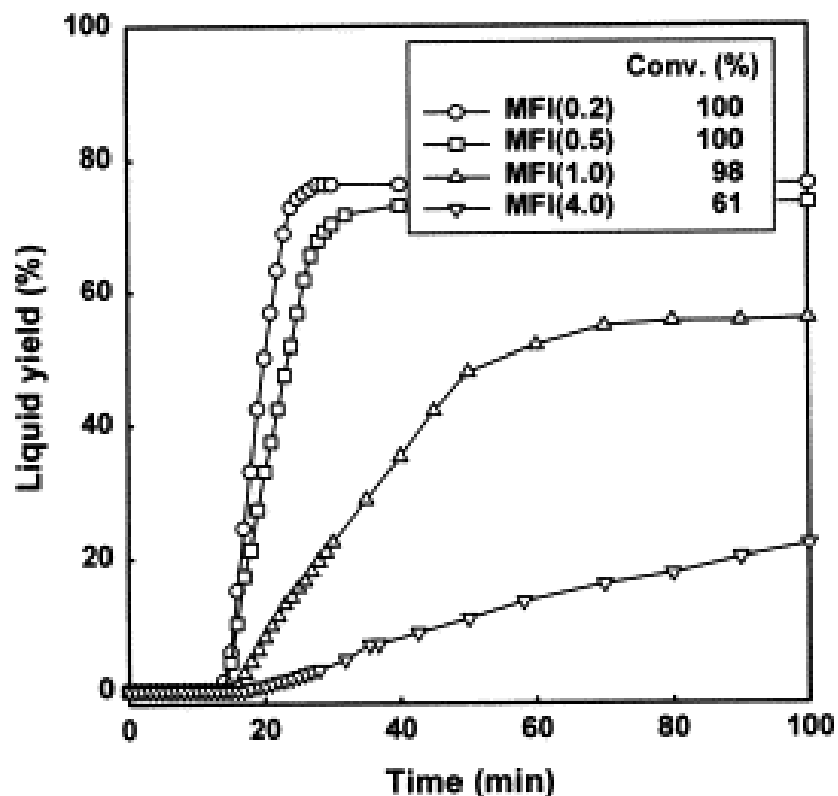
## 산특성의 영향 – Si/Al 비 (HZSM-5), Park et al.

Table Product distribution (wt%) in the catalytic degradation of polyethylene at 450°C for 1h [Ref. 62]

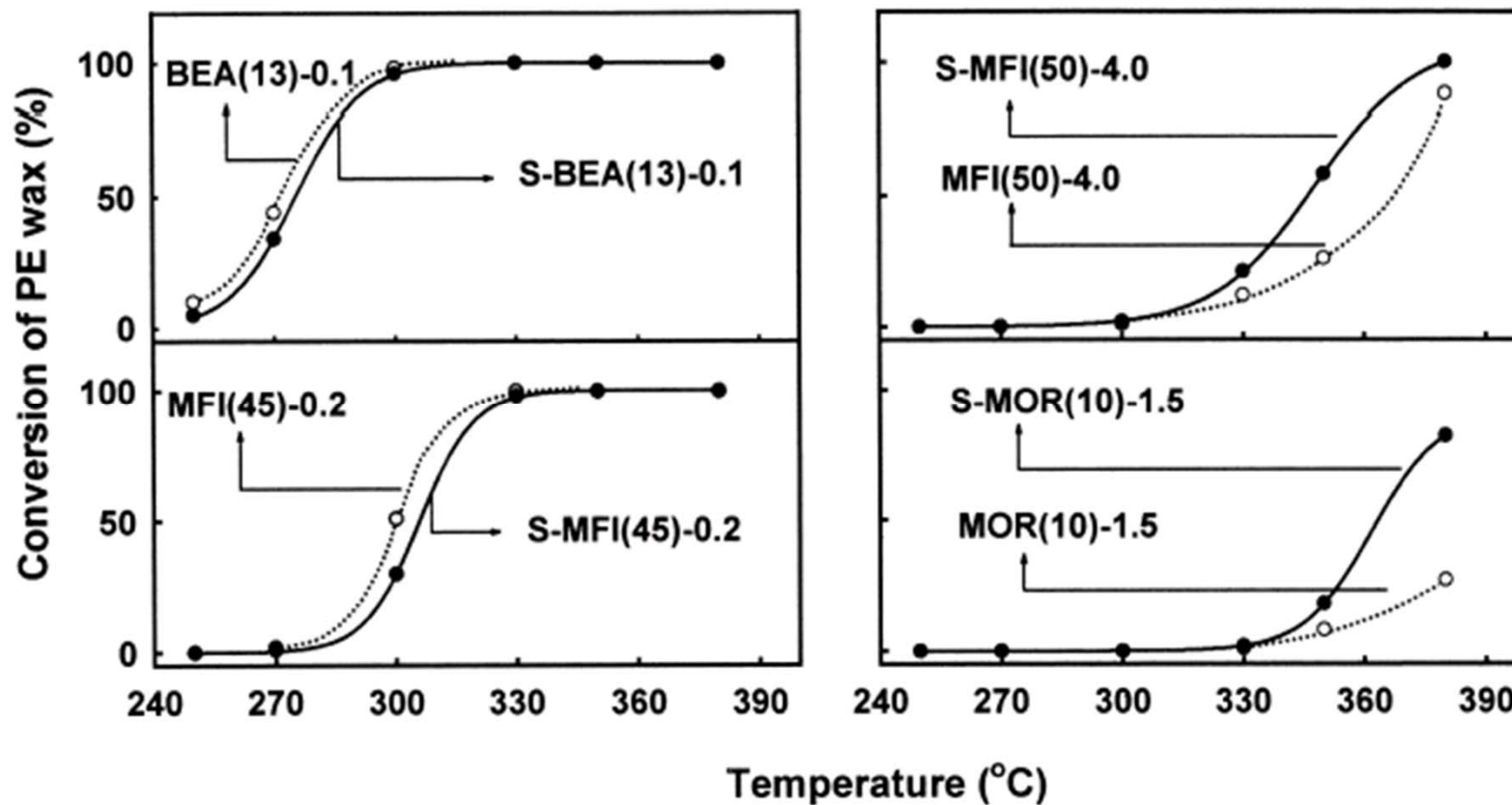
Catalysts	Gas	Liquid	Residue	RON
HZSM-5(22 <sup>a</sup> )	88.4	10.9 (aromatics:75.6wt%)	0.7	93.3
HZSM-5(44 <sup>a</sup> )	78.5	21.5 (aromatics:50.7wt%)	0	85.1

<sup>a</sup> Si/Al ratio

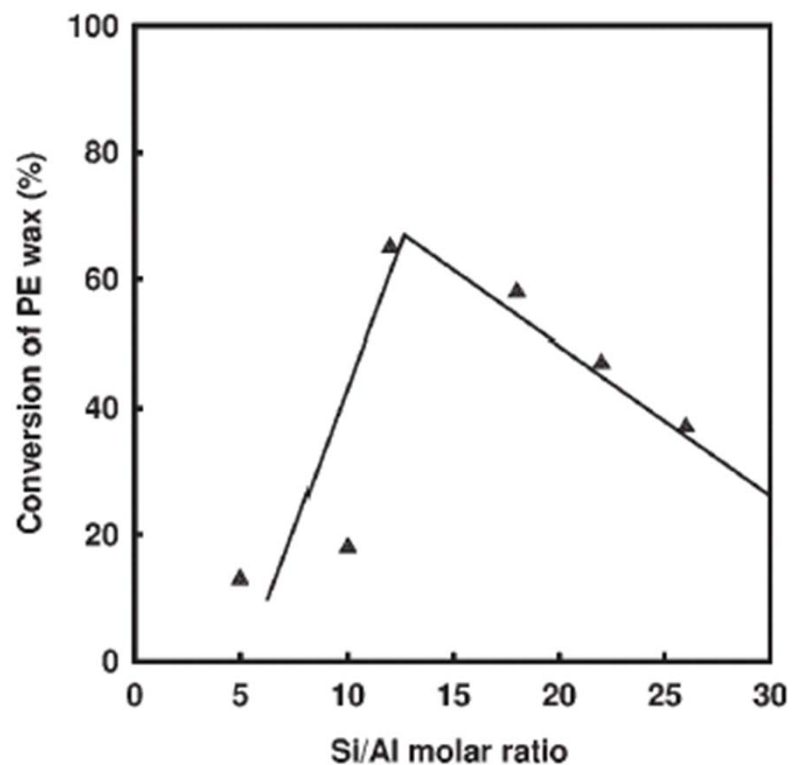
# 입자크기 영향, Seo et al.



## 외표면 차폐영향 - 실리카 처리, Seo et al.



## 산특성의 영향 – 외부 표면 Si/Al 비 (Mordenite), Seo et al.



Si/Al = 5 인 MOR을 염산으로 처리하여 알루미늄을 용출시켜 제조

Figure 6. Effect of the Si/Al molar ratio on the conversion of PE wax in the catalytic degradation over the MOR catalysts at 380 °C.

# 외표면적의 영향 (n-HZSM-5 > HZSM-5)

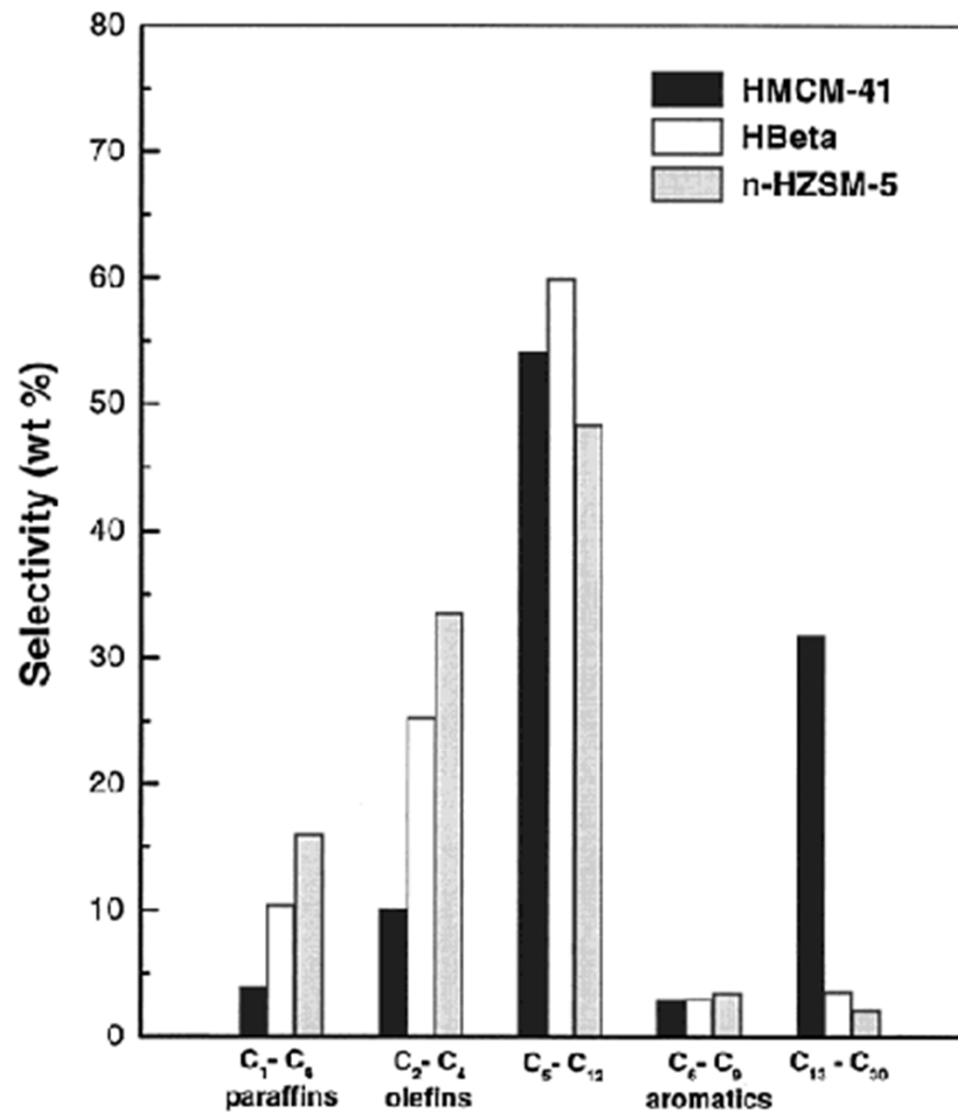
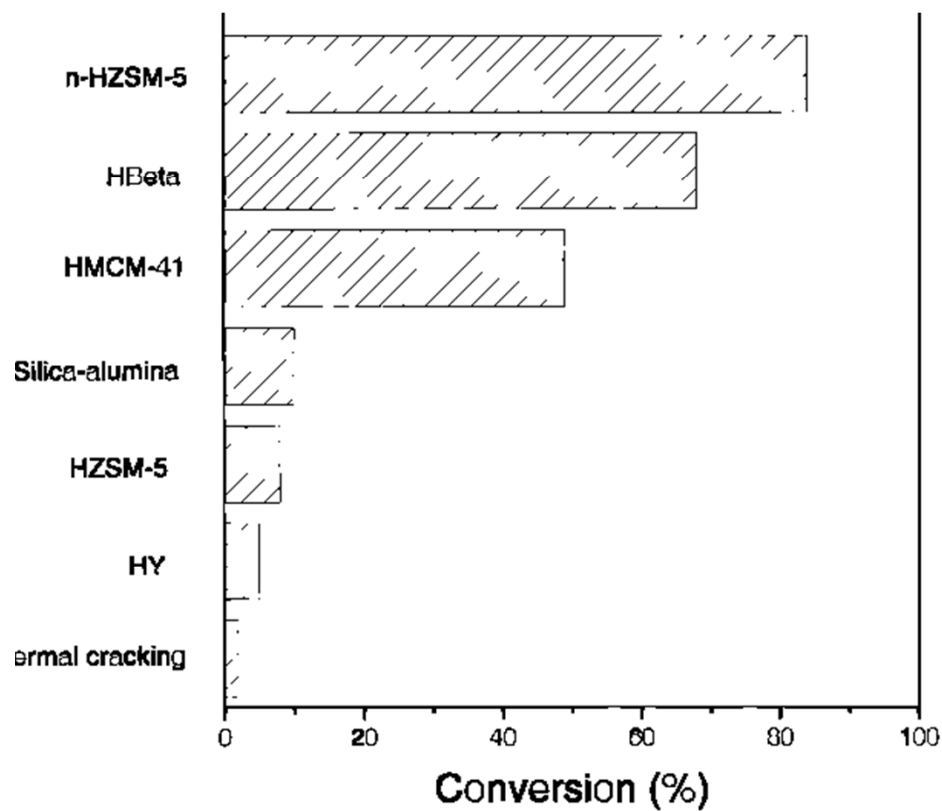
Table 1. Physicochemical and Textural Properties of the Catalysts

catalyst	n-HZSM-5	HZSM-5	HBeta	HY	HMCM-41	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
Si/Al	24	31	39	3	45	36
pore size (nm)	0.55	0.55	0.64	0.74	2.4	2-12
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	430	361	613	583	1164	261
external surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	81	7	25	9	73	—
pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	0.48	0.18	0.35	0.26	0.79	0.97
micropore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	0.15	0.17	0.24	0.23	—	—
crystal size (μm)	0.075	3	0.20	0.50	0.2-2	—
acidity (mequiv of NH <sub>3</sub> g <sup>-1</sup> ) <sup>c</sup>	0.38	0.52	0.32	0.37	0.22	0.24
T <sub>max</sub> (°C) <sup>c</sup>	462	470	422	300	338	302

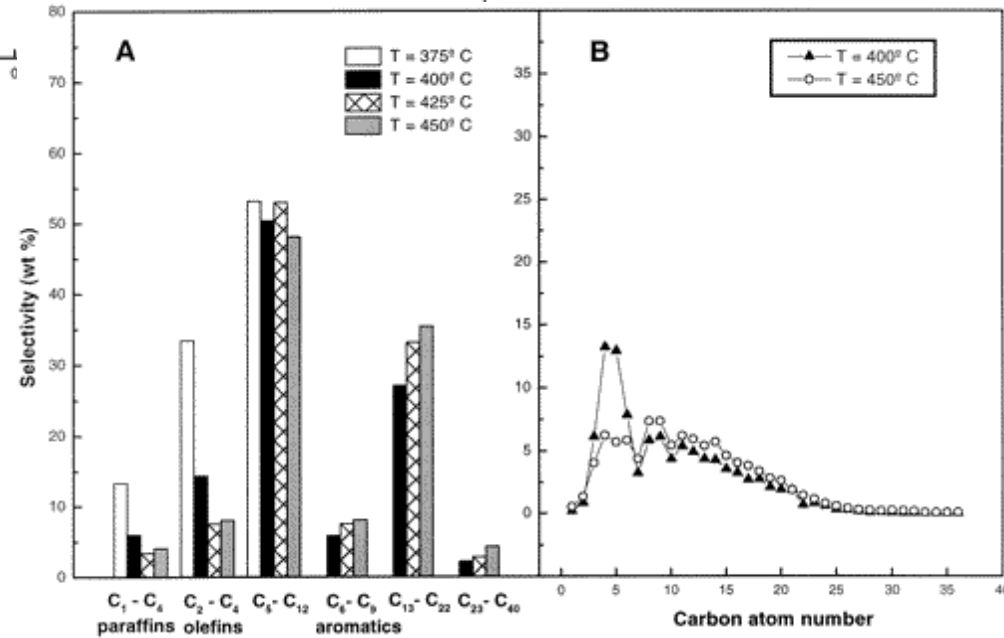
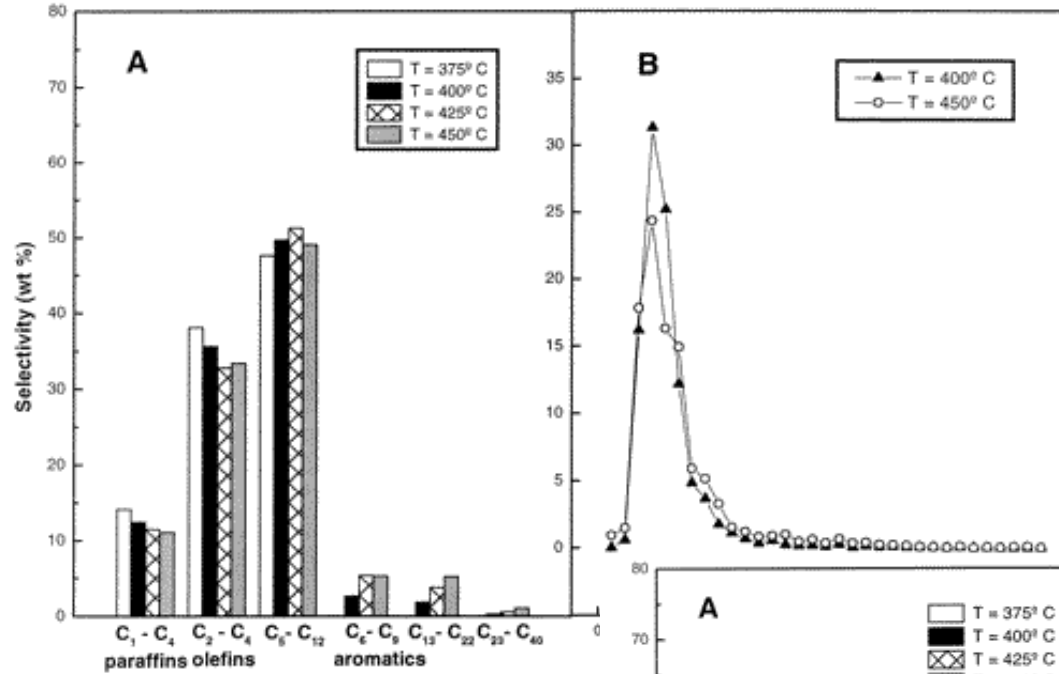
<sup>a</sup> Obtained by application of the t-plot method. <sup>b</sup> Measured at  $p/p_0 = 0.995$ . <sup>c</sup> From ammonia TPD.



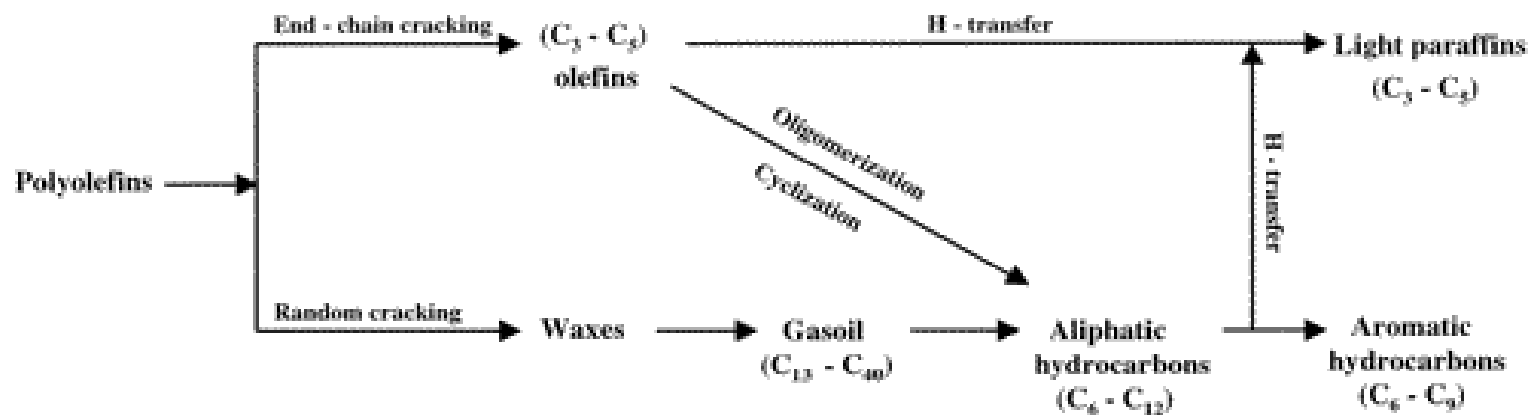
# 외표면적의 영향 (n-HZSM-5 > HZSM-5)



# Plastic mixture (MCM-41, nHZSM-5)



## Plastic mixture (MCM-41, nHZSM-5)



## 외표면적의 영향 (반응물 : PP – Corma et al.)

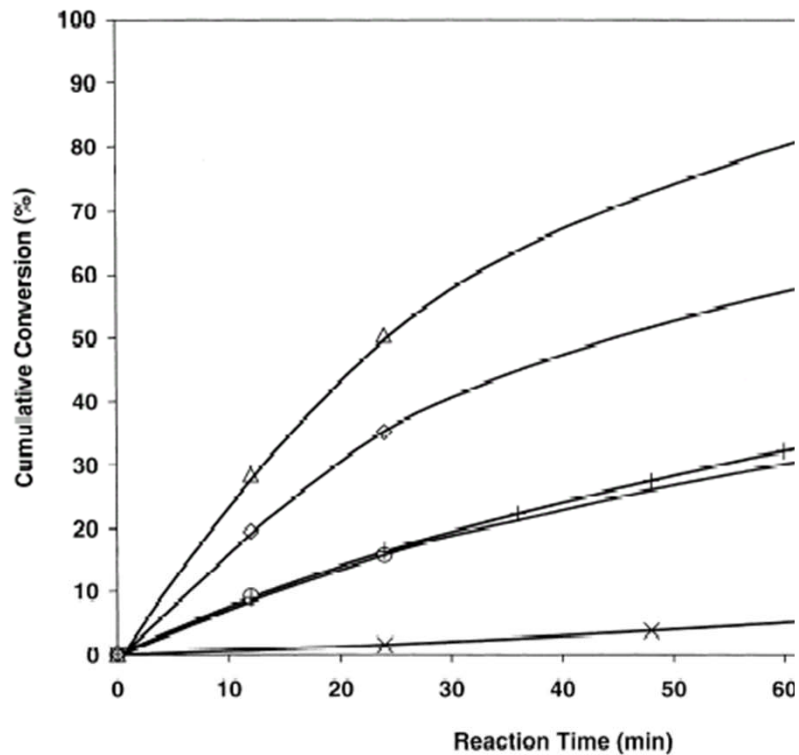


Fig. 2. Catalytic cracking of PP at 380°C with zeolites (plastic/catalyst = 35/1.5 w/w): H-USY 500 (○), H-USY 500-SC (+), H-USY 712 (△) and H-USY 760 (◇). Thermal cracking (×) for comparison.

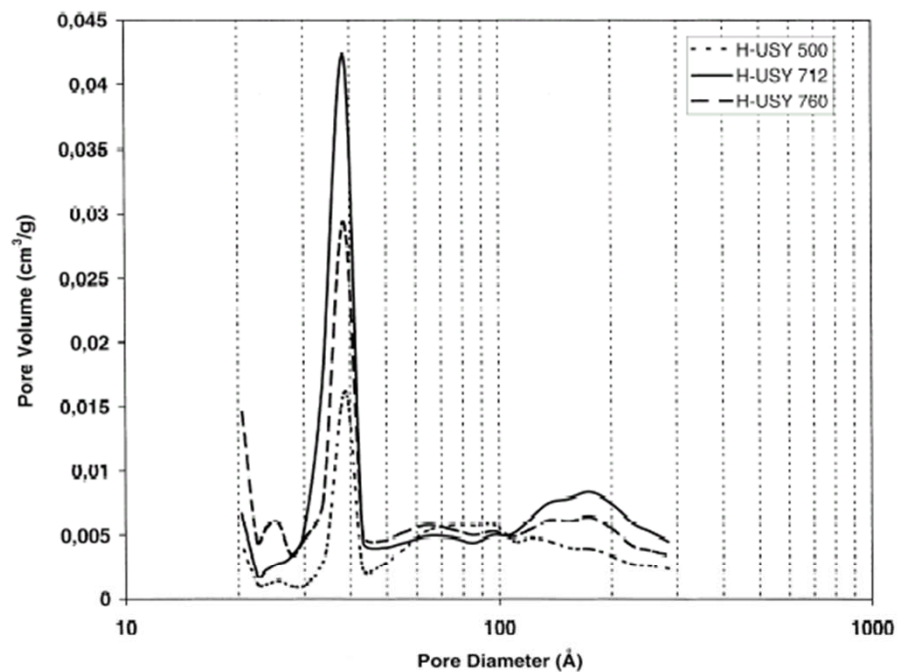


Fig. 3. Pore size distribution of zeolites in the mesoporous range.

# HMCM-41, silica-alumina 및 폐촉매 결과

[반응물 : PP – Corma et al.]

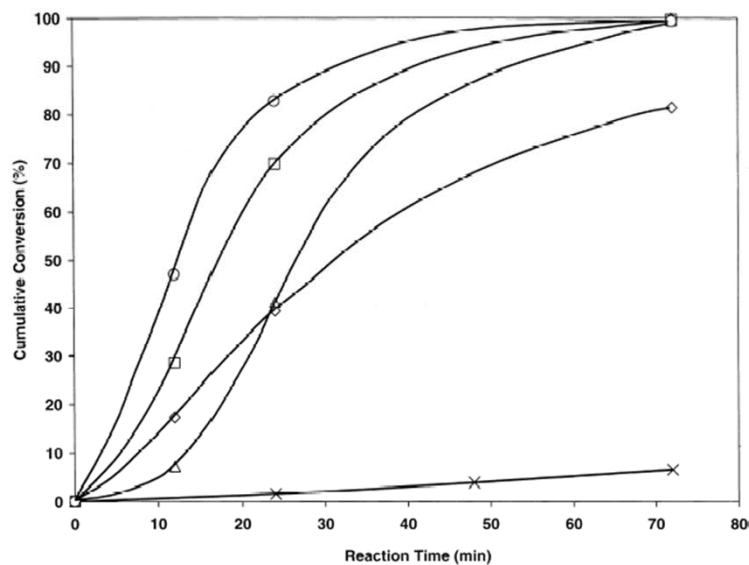


Fig. 4. Catalytic cracking of PP at 380°C with mesoporous catalysts (plastic/catalyst=35/1.5 w/w): MCM-41 (○), Si-Al 13% (□), 25% (Δ) and MSA (◇). Thermal cracking (×) for comparison.

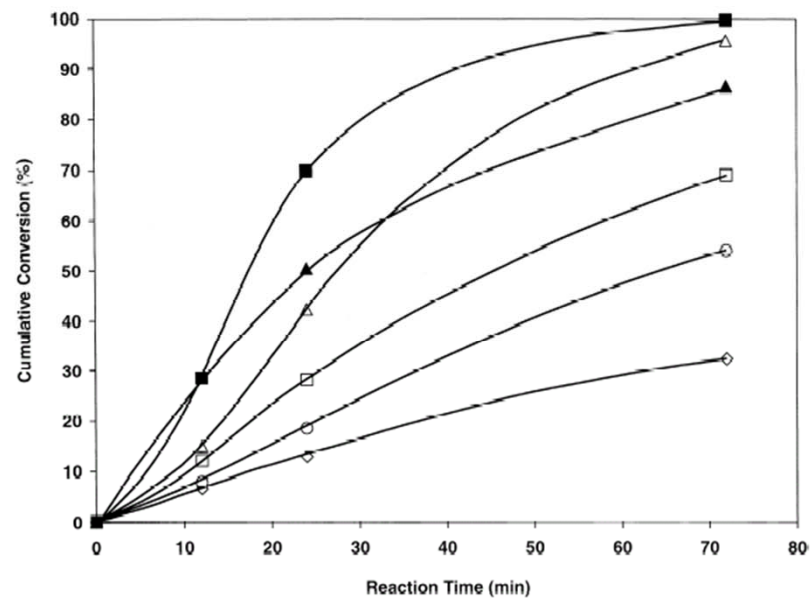


Fig. 5. Catalytic cracking of PP at 380°C with Resoc-g using various amounts of catalyst (plastic = 35 g): 1 g (◇), 1.5 g (○), 1.75 g (□) and 2 g (Δ). Si-Al 13% (■) and H-USY 712 (▲) have been represented for comparison (plastic/catalyst=35/1.5 w/w).

## LDPE로 부터 olefin 생성 – Zhibo et al.

Table Fractions of oils from polyethylene on solid acids and bases [Ref. zhibo et al-catalysis today]

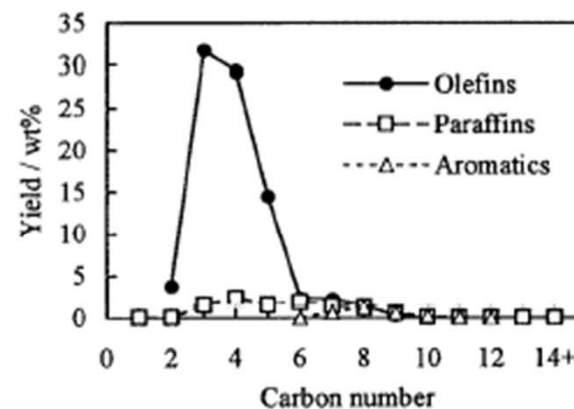
Components	Catalytic degradation (wt%)			Thermal degradation (wt%)
	HZSM-5	silica-alumina	ZnO	
1-olefins	7	4	34	24
n-paraffins	12	30	51	44
Aromatics	35	13	0	3
Others	46	53	15	30

## LDPE로 부터 olefin 생성 (H-Borosilicate)– Uemichi et al.

**Table 1.** Yields of products obtained from degradation of LDPE at 525 °C

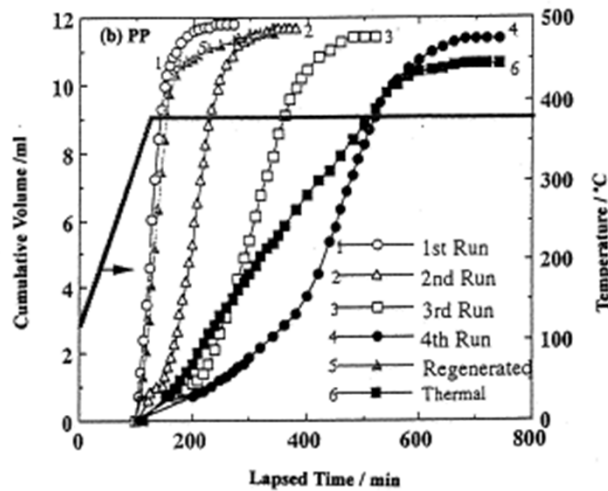
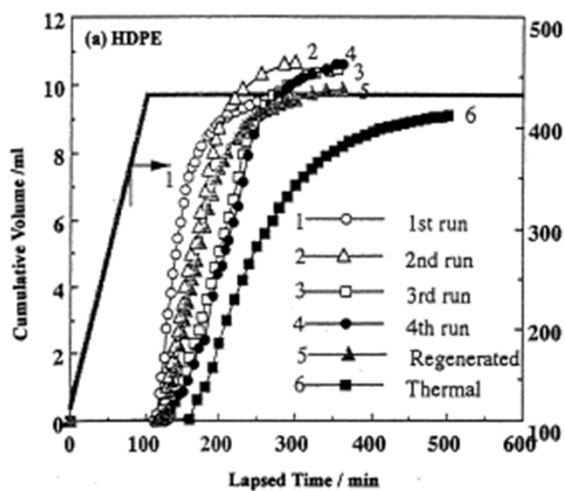
Yield / wt%	Catalyst			
	H-B-silicate	H-ZSM-5	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Thermal
H <sub>2</sub>	0.1	0.3	0.2	tr. <sup>a</sup>
C <sub>1</sub> +C <sub>2</sub>	3.9	9.4	1.3	2.5
C <sub>3</sub> -C <sub>5</sub> olefins	75.5	40.2	53.3	5.1
C <sub>3</sub> -C <sub>5</sub> paraffins	5.2	21.9	9.7	1.7
C <sub>6</sub> + aliphatics	12.2	7.4	27.8	11.4
Aromatics	3.0	20.8	6.8	tr. <sup>a</sup>
Wax	0.2	0	0	79.3
Coke	tr. <sup>a</sup>	tr. <sup>a</sup>	0.9	tr. <sup>a</sup>

<sup>a</sup>Less than 0.05%.

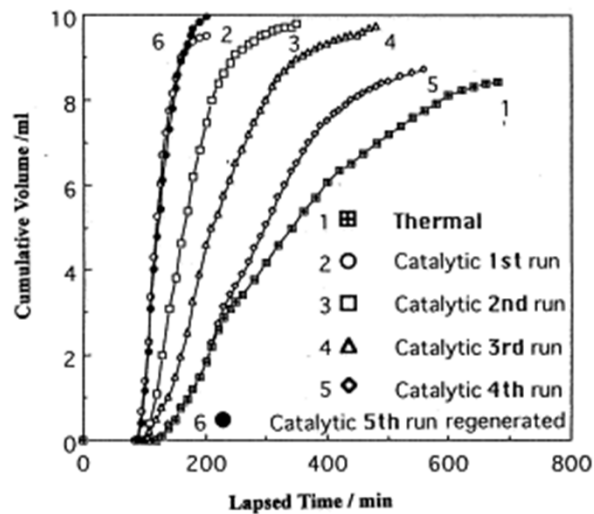


**Figure 1.** Carbon number distributions of the products obtained from degradation of LDPE over H-borosilicate at 525 °C.

# 비활성화 (FSM, Silica/Alumina)



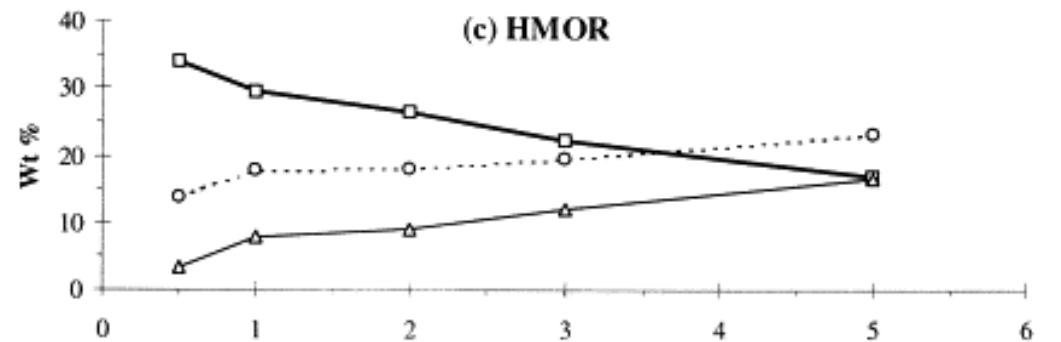
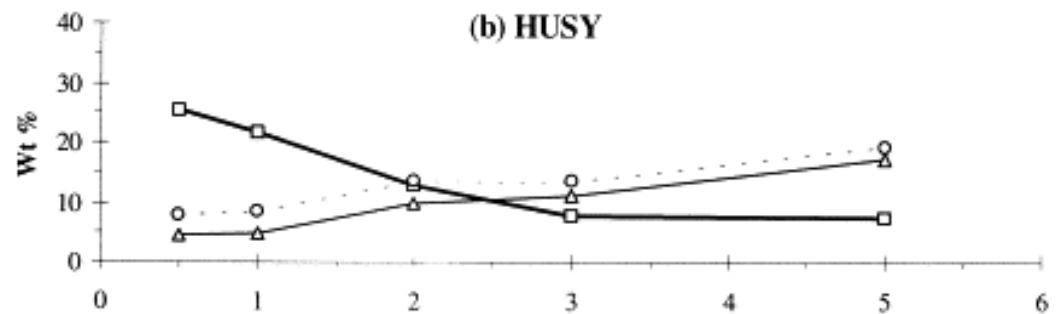
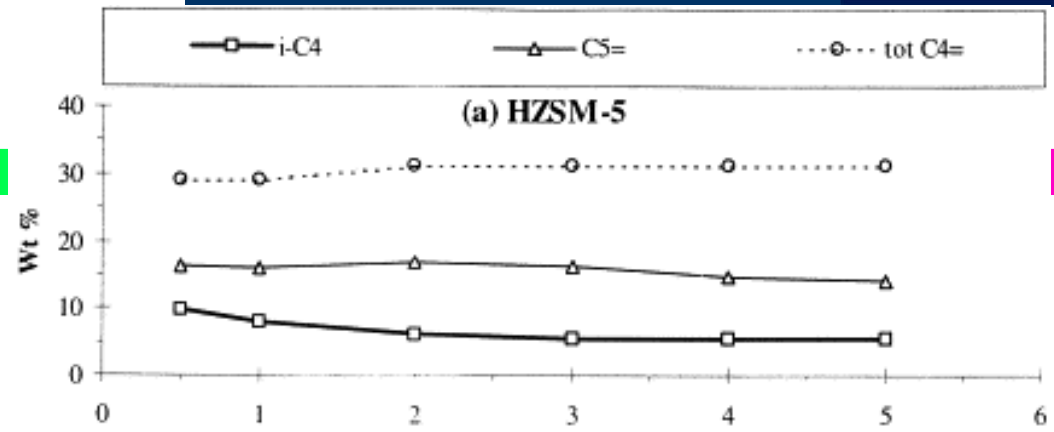
FSM 촉매



Silica/Alumina



# 비활성화 (PE)



# PS 촉매 열분해

Table Selectivity of aromatics formed in the degradation of PS at 400°C for 2h [천연제 올라이트]

Aromatics	Thermal	NZ	HNZ	SCLZ	HSCLZ	HZSM-5	Silica-alumina
Benzene	0.04	0.15	0.18	0.06	0.05	1.1	1.9
Toluene	5.7	5.2	6.3	6.7	6.0	6.4	4.7
Ethylbenzene	6.6	10.1	12.8	8.0	16.2	10.5	22.6
Xylene	0.01	0.02	0.02	0.02	0.03	0.14	0.01
Styrene	52.2	50.8	48.1	53.2	47.7	50.7	36.1
Iso-propylbenzene	1.6	2.5	2.8	1.9	2.9	2.1	0.04
o-methylstyrene	7.9	7.3	9.2	7.8	7.7	8.4	7.6
trimethylbenzene	0.25	0.26	0.03	0.34	0.29	0.34	0.40
Indane	0.01	0.30	0.01	0.01	0.08	0.12	0.05
C10-C15	0.19	0.37	0.65	0.37	0.55	1.2	1.5
C16-C21	17.3	16.0	13.7	15.8	14.2	13.2	19.2
C22-C30	8.2	7.0	6.3	5.8	4.3	5.8	5.9

# PS 촉매 열분해 (염기촉매)

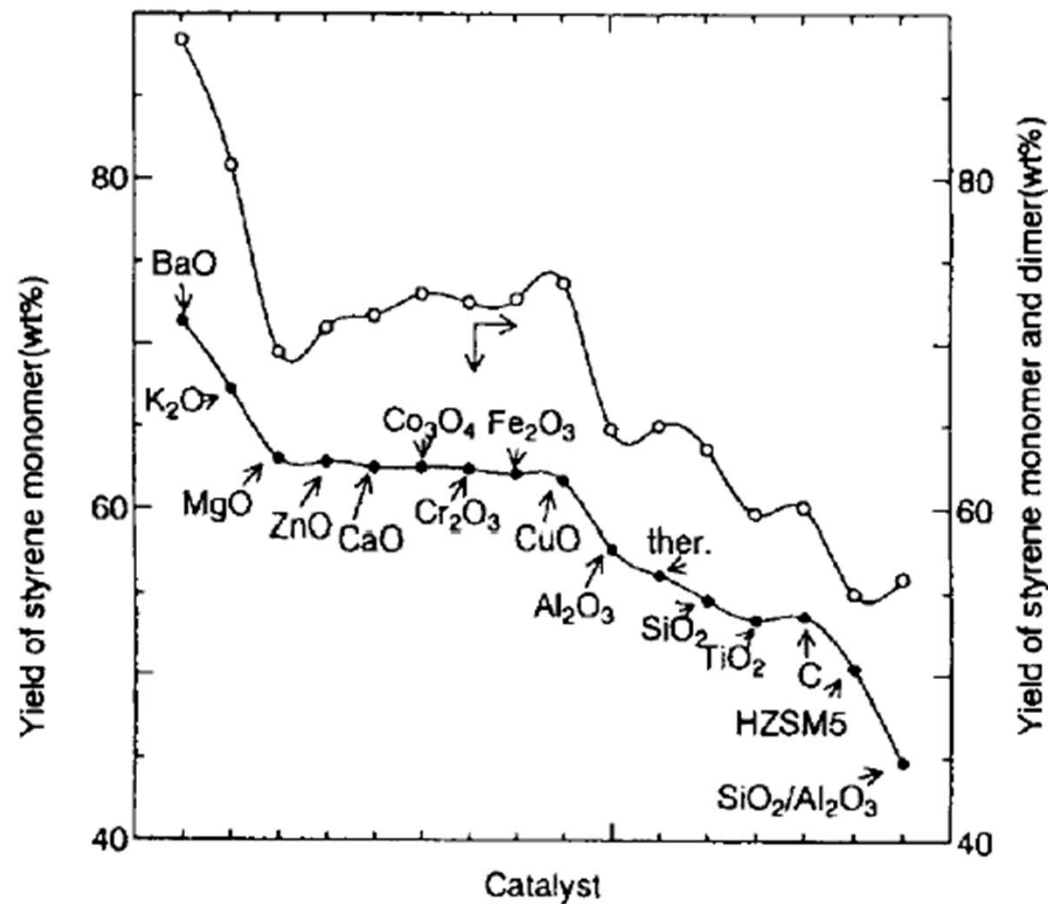


Fig. 2. Recovery of styrene monomer from polystyrene on various catalysts.



## 기타 연구된 촉매

- Clay, Al-Clay
- SAPO-37, natural zeolite (경상북도 영일), 폐촉매
- Activated carbon
- Titania, Ti-Beta

# Summary

- ❖ 촉매의 다양한 구조와 기공 크기는 분해활성에 영향을 미친다.
- ❖ 분자 크기가 큰 플라스틱의 촉매 반응시 처음으로 분해가 되는 촉매 외표면이 매우 중요
- ❖ HZSM-5 : 강한 산점으로 인한 분해반응 활성 우수,  
기상 생성물 많음, 코크 생성 억제
- ❖ MCM-41 : 중간세기 산점과 큰 기공으로 인하여 활성이 우수  
가솔린 범위와 middle distillate 범위 탄화수소 생성
- ❖ 폐촉매 : 경제적인 관점에서 많은 가능성 제시
- ❖ H-Ga-silicate : 방향족(BTX) 생성에 탁월한 성능
- ❖ PS 분해시 스티렌 단량체를 얻기 위해서는 염기촉매 (BaO), 에틸벤젠등을 얻기 위해서는 산촉매 선정