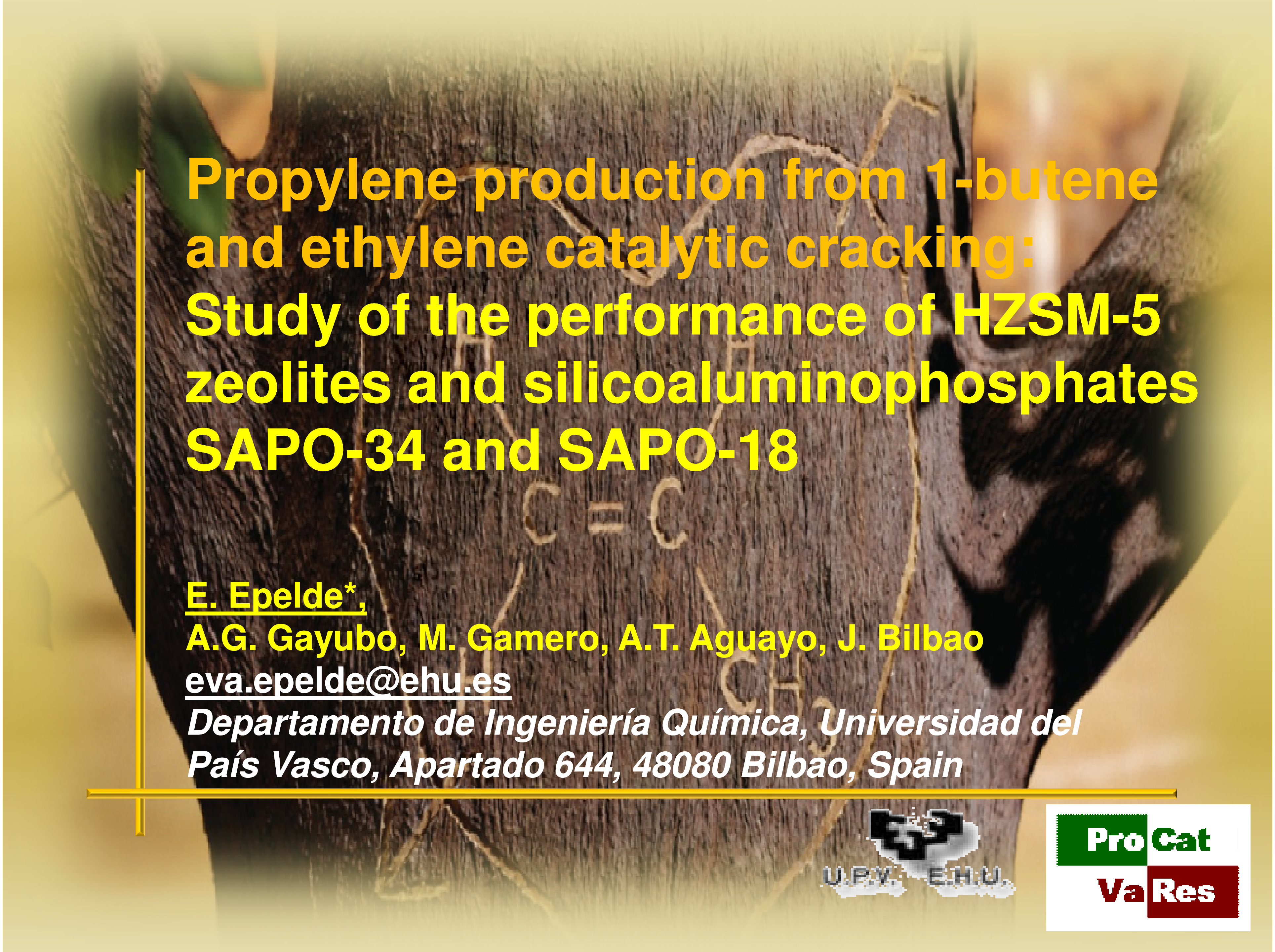

Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and silicoaluminophosphates SAPO-34 and SAPO-18

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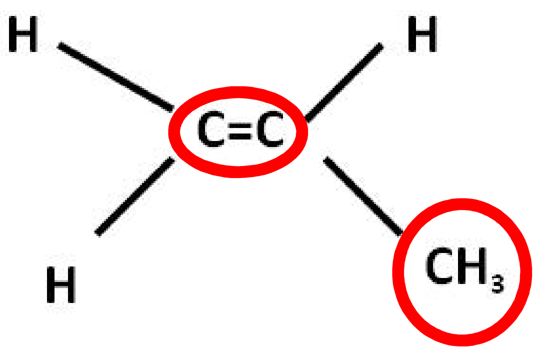
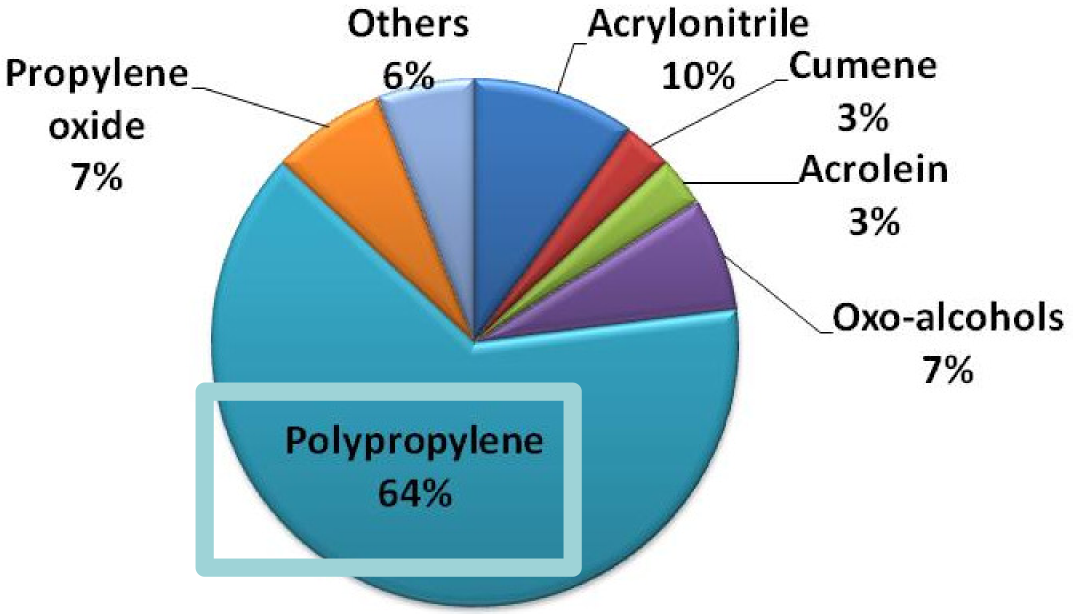
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

❖ **Propylene:** key building block for the production of important petrochemicals





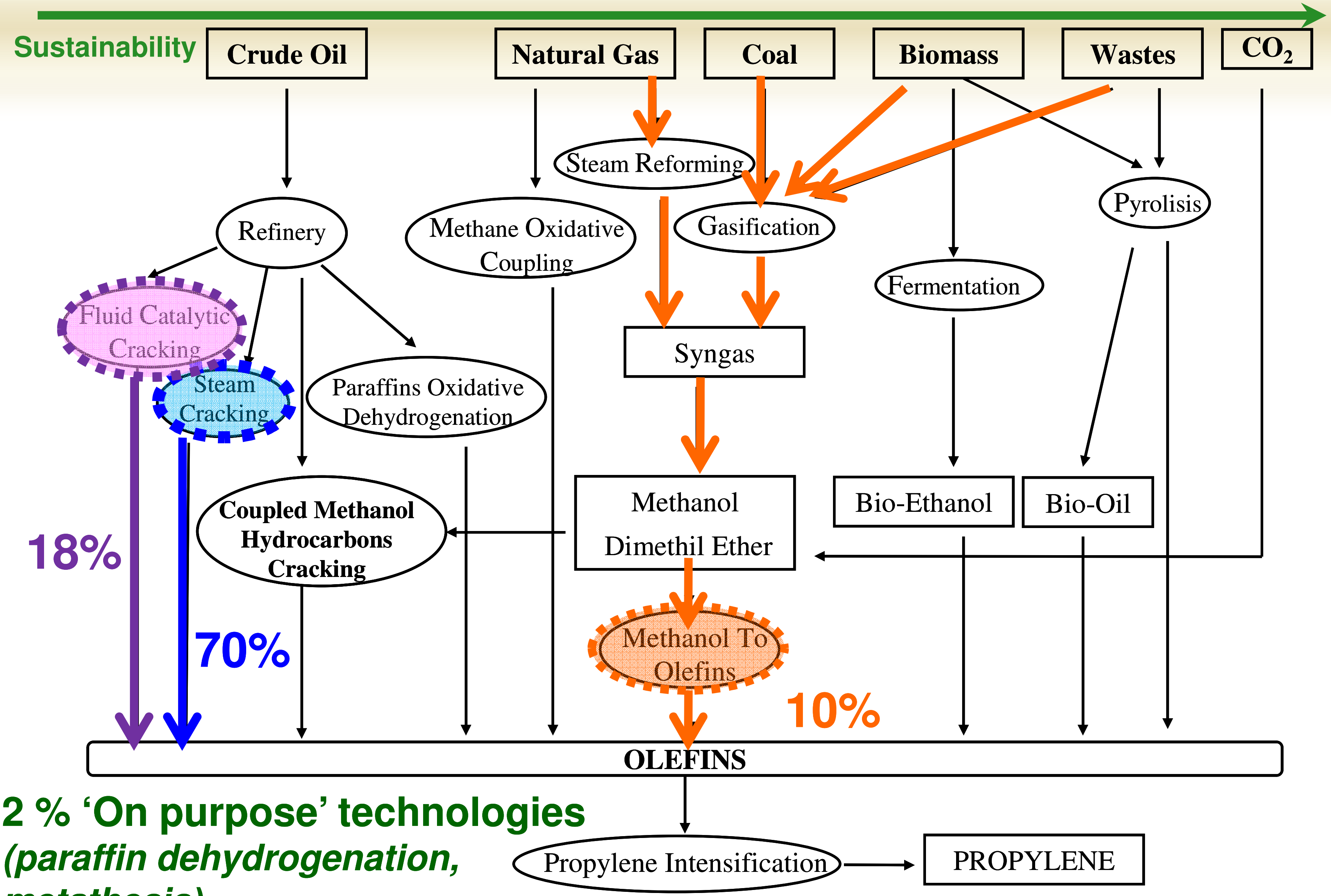
✓ C-C double bond
✓ Adjacent methyl group

J.S. Plotkin ,*Catalysis Today* ,106 (2005) 10–14

❖ Propylene **worlwide demand** has been increasing at an annual average of 5.7% and by year 2015, demand will grow to 105 million tonnes

T. Mokrani and M. Scurrell, *Catalysis Reviews*, 51 (2009),1

Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs



Sustainability

Crude Oil

Natural Gas

Coal

Biomass

Wastes

CO_2

Steam Reforming

Gasification

Pyrolisis

Refinery

Methane Oxidative Coupling

Fermentation

Fluid Catalytic Cracking

Steam Cracking

Paraffins Oxidative Dehydrogenation

Syngas

Coupled Methanol Hydrocarbons Cracking

Methanol

Dimethil Ether

Bio-Ethanol

Bio-Oil

18%

70%

Methanol To Olefins

10%

OLEFINS

Propylene Intensification

PROPYLENE

2 % ‘On purpose’ technologies

(paraffin dehydrogenation, metathesis)

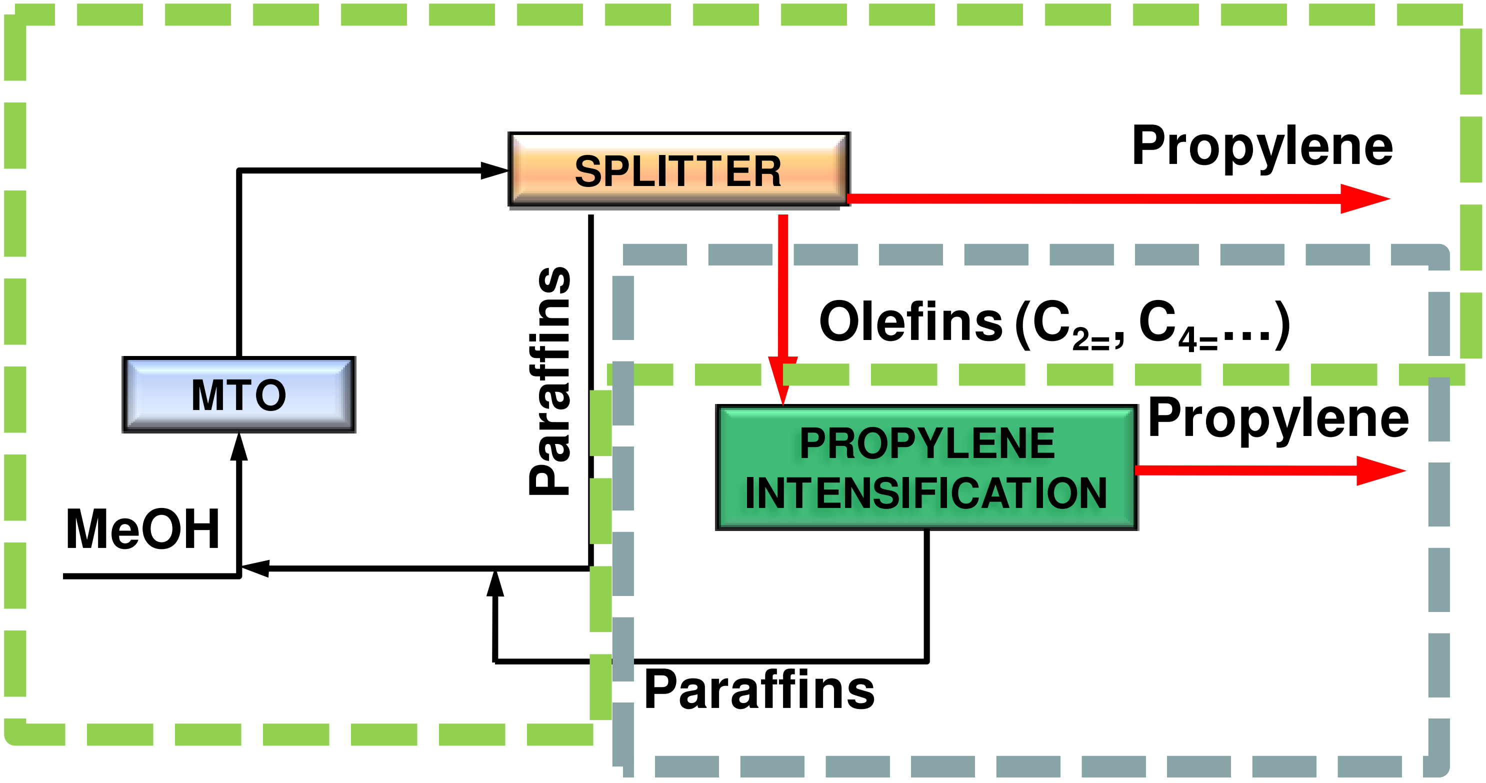
D. Mier et al. *Chemical Engineering Journal*, 160 (2010) 760-769

Pro Cat
Va Res

Catalytic Processes and Waste Valorization

U.P.V. E.H.U.

www.ehu.es/cpwv



C_2-C_4 olefin interconversion

- ✓Acid catalysts ➔ Mechanism of oligomerization-cracking
- ✓ Shape selectivity of the catalysts significant role in propylene yield and selectivity

New catalyst development for C_2-C_4 olefin catalytic cracking

- ✓ Modification of HZSM-5
  - ✓ by metal incorporation (P, P-La, Ni, K…)
  - ✓ by dealumination methods (NaOH, steaming…)
- ✓ Silicoaluminophosphates (SAPO-34, SAPO-18)

Aim of this work: Study the role of the properties of the catalyst (acidity and shape selectivity) in the intensification fo propylene production from 1-butene and ethylene transformation

Conversion-propylene yield **selectivity-stability**

X. Zhu, S. Liu, Y. Song, L. Xu, *Catal. Lett.*, 103 (2005) 201-210
G. Zhao, J. Teng, Z. Xie, W. Jin, W. Jang, Q. Chen, Y. Tang, *J. Catal.*, 248 (2007) 29-37
A.T. Aguayo, D. Mier, A.G. Gayubo, M. Gamero, J. Bilbao, *Ind. Eng. Chem. Res.*, 49 (2010)

Catalyst preparation

Active phase ⇨

Zeolite
HZSM-5 or
SAPOs

(25 %)

Wet extrusion,
dry, calcination
(550 ºC, 2h)

⇧ ⇧

Bentonite
(30 %)

Alumina
(45 %)

⇨ **Catalyst**

HZ-30 ($SiO_2/Al_2O_3=30$)
HZ-80 ($SiO_2/Al_2O_3=80$)
HZ-280 ($SiO_2/Al_2O_3=280$)
SAPO-18
SAPO-34

✓**Confer suitable size and mechanical resistance to the catalytic particles in fixed and fluidized bed reactors**

✓**A matrix with meso- and macroporous structure is formed**

- **reducing deactivation by coke**
- **increasing hydrothermal stability**

A.T. Aguayo, A.G. Gayubo, R. Vivanco, M. Olazar, J. Bilbao, *Appl. Catal. A.: Gen. 283* (2005) 197

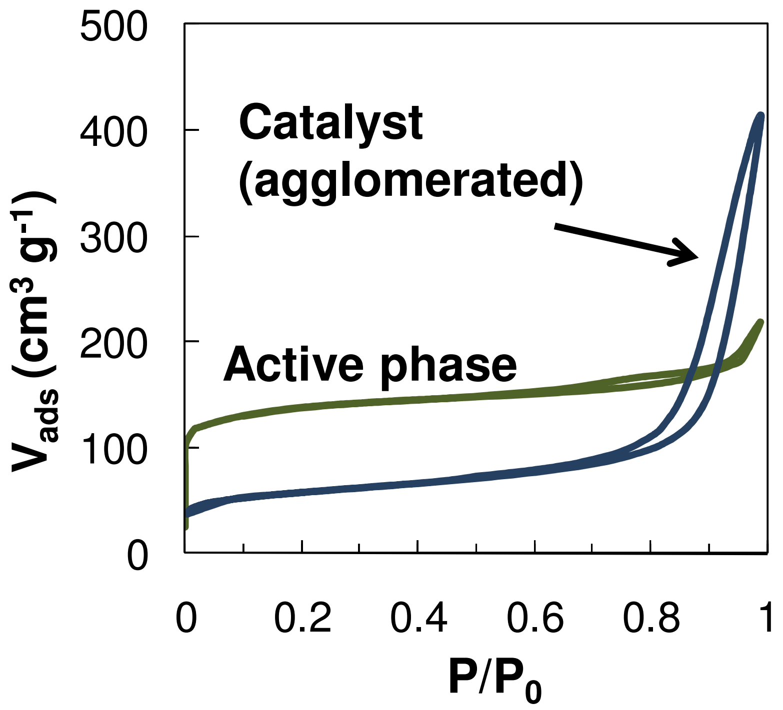
INTRODUCTION
EXPERIMENTAL
RESULTS
CONCLUSIONS

Catalyst characterization

N_2 adsorption-desorption (77 K)

Active phase	S_{BET} (m^2/g)	$V_{mesopore}$ (cm^3/g)	$V_{micropore}$ (cm^3/g)
HZ-30	448	0.15	0.12
HZ-80	556	0.11	0.10
HZ-280	512	0.10	0.16
SAPO-18	797	0.08	0.28
SAPO-34	611	0.06	0.24

Catalyst	S_{BET} (m^2/g)	$V_{mesopore}$ (cm^3/g)	$V_{micropore}$ (cm^3/g)
HZ-30	202	0.53	0.042
HZ-80	209	0.48	0.036
HZ-280	231	0.38	0.048
SAPO-18	236	0.23	0.072
SAPO-34	215	0.20	0.046

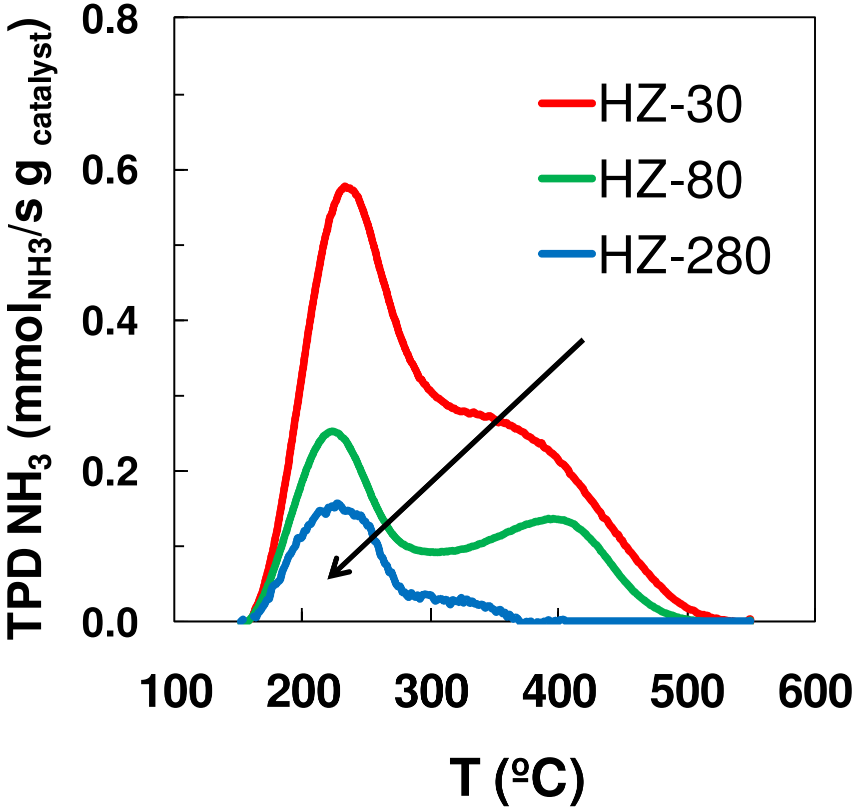


INTRODUCTION
EXPERIMENTAL
RESULTS
CONCLUSIONS

Catalyst characterization

DSC (150 ºC)-
TPD of NH_3 (up to 550 ºC)

Active phase	Total acidity (mmol NH_3 g^{-1})	*T* peak(°C) in the TPD	
		1st peak	2nd peak
HZ-30	1.07	230	340
HZ-80	0.46	210	395
HZ-280	0.15	227	325
SAPO-18	0.37	243	335
SAPO-34	0.64	258	348

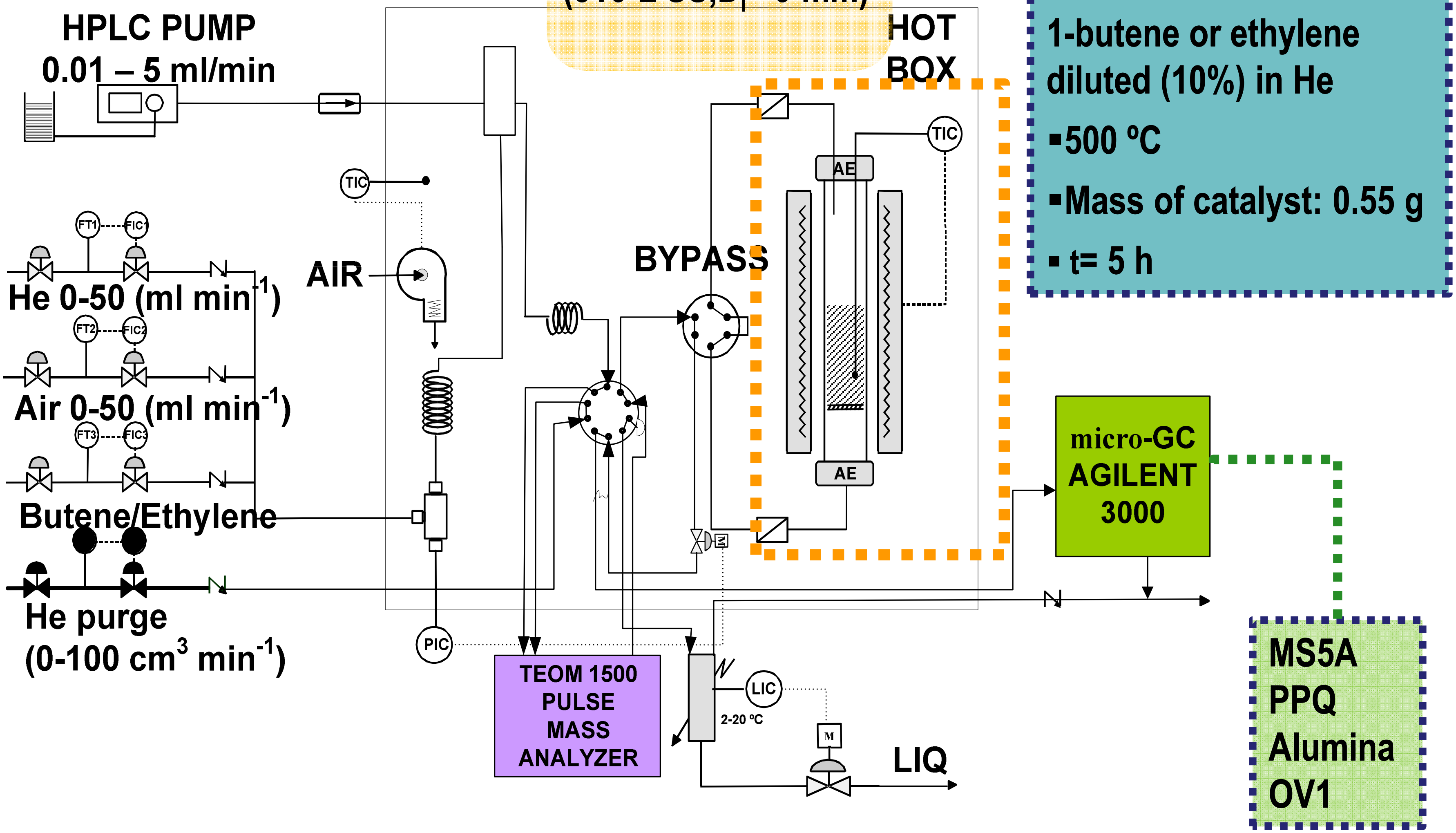


These acid properties remain after agglomeration

Reactor setup

Fixed bed reactor
Microactivity
(316-L SS,D_i= 9 mm)

- **Feed: 35 cm^3 min^{-1} of 1-butene or ethylene diluted (10%) in He**
- **500 ºC**
- **Mass of catalyst: 0.55 g**
- **t= 5 h**



INTRODUCTION
EXPERIMENTAL
RESULTS
CONCLUSIONS

Evaluation criteria used for catalytic performance

☐ **Conversion (X):**

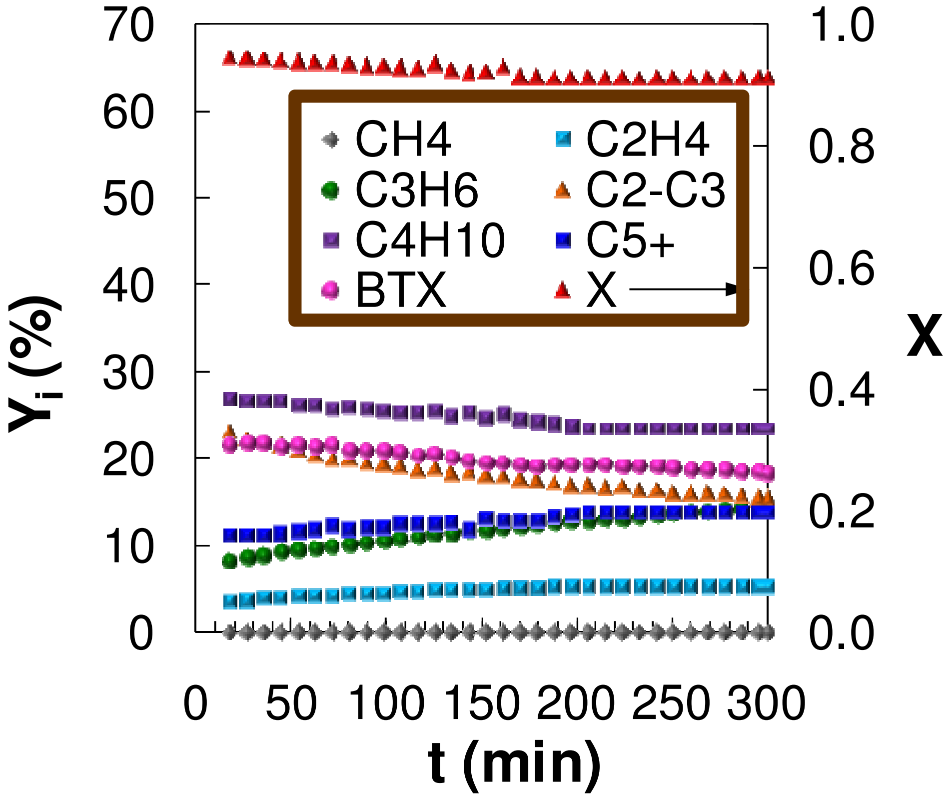
$$X = \frac{F_0 - F}{F_0}$$

☐ **Yield of i lump:**

$$Y_i = \frac{F_i}{F_0}$$

☐ **Selectivity of i lump:**

$$S_i = \frac{F_i}{F_0 - F}$$



Molar flowrates:

F_0= reactant in the feed

F= reactant in the outlet stream

F_i= i-lump in the product stream

HZ-30 catalyst

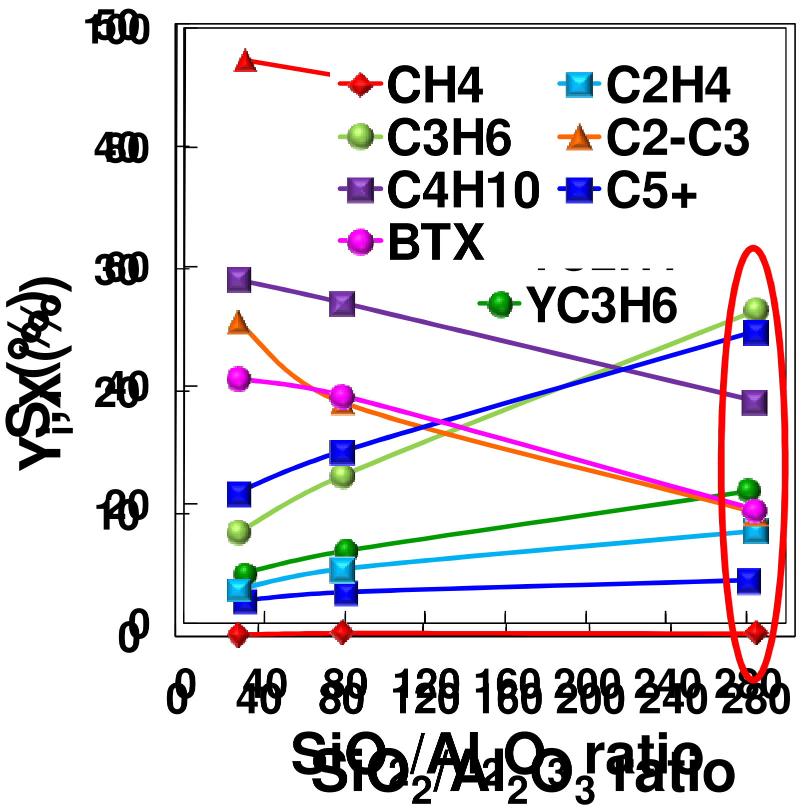
500 º C, W/F_{A0}=24.5 g catalyst h (mol CH_2)$^{-1}$

Terms expressed as CH_2 equivalent units, corresponding to zero time on stream

Transformation of 1-butene

HZ-280

Effect of SiO_2/Al_2O_3 in HZM-5 zeolites

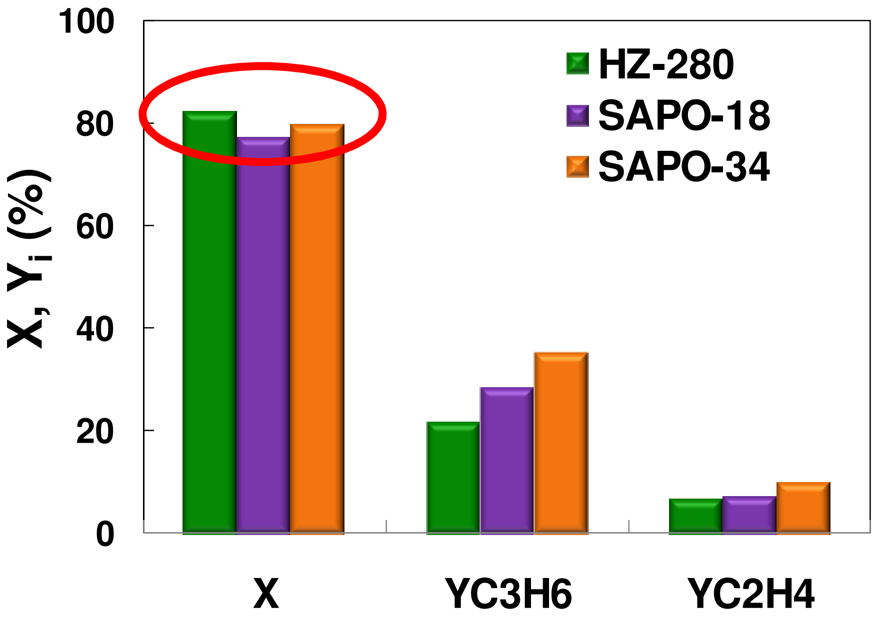


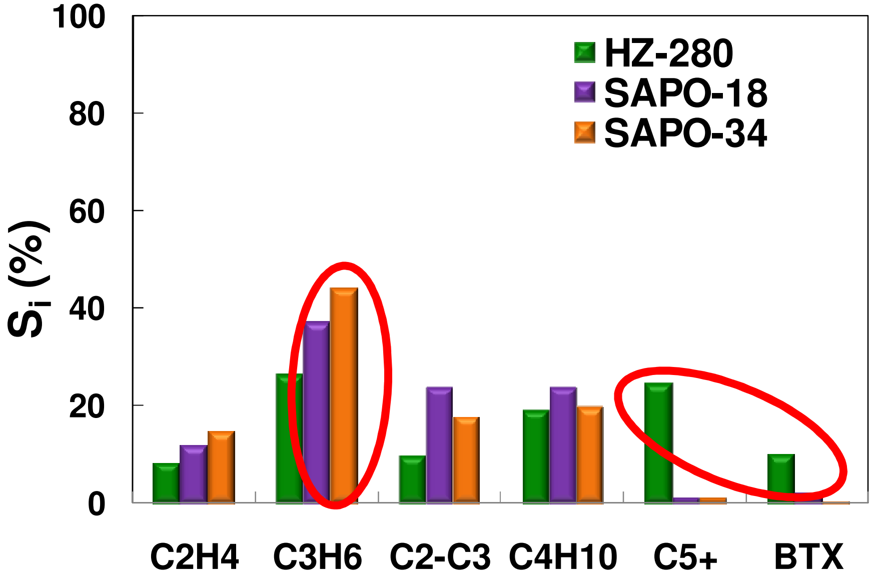
- ❑ SiO_2/Al_2O_3 ratio ↑
- ✓ Butene conversion ↓
- ✓ C_2H_4 and C_3H_6 yield ↑
- ✓ C_2H_4, C_3H_6 and C_{5+} selectivities ↑
- ✓ Hydrogen transfer reactions (catalyzed by strong acid sites) ↓
- ✓ C_2-C_4 and BTX selectivities ↓

INTRODUCTION
EXPERIMENTAL
RESULTS
CONCLUSIONS

Transformation of 1-butene

Shape selectivity catalysts



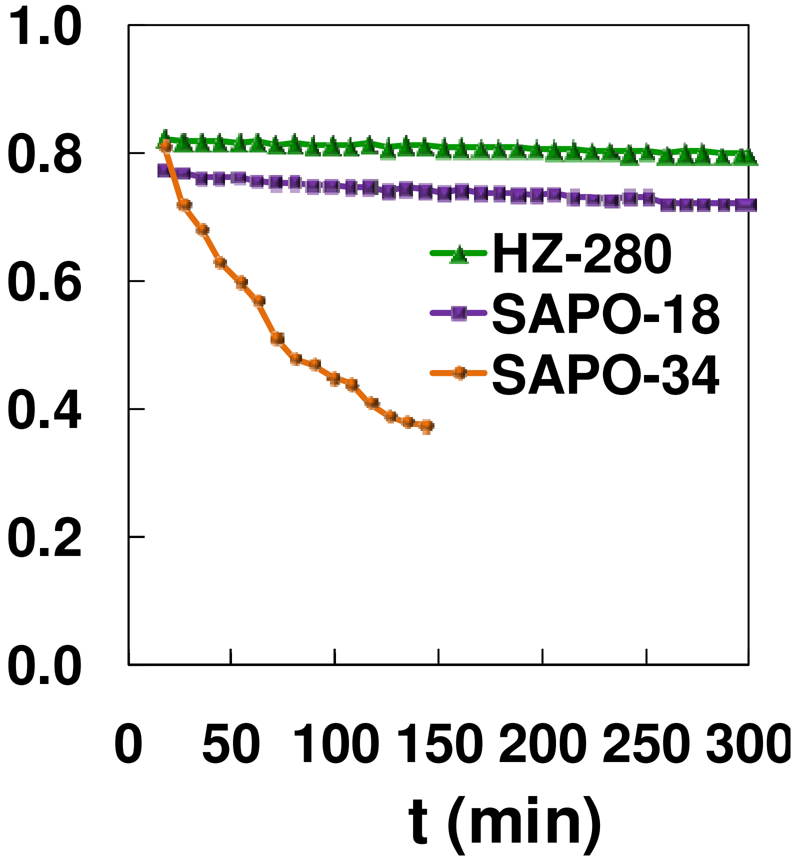


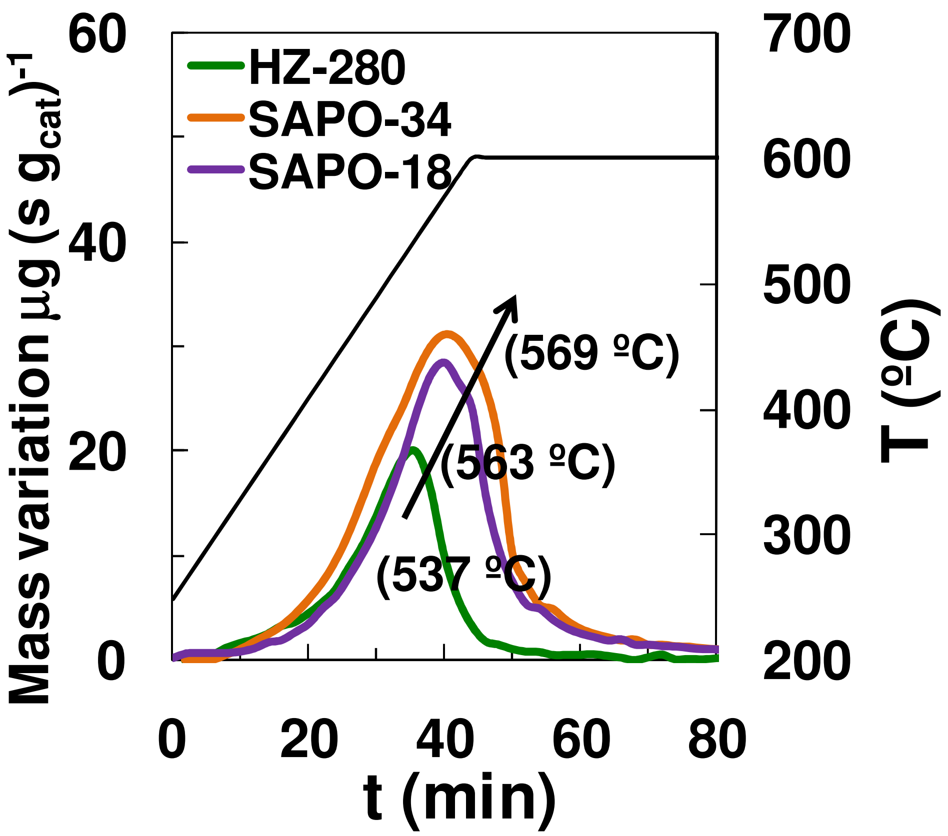
- ✓ **Severity of shape selectivity is higher for SAPOs (steric limitations)➔ SC_3H_6 ↑**
- ✓ **SAPO-34 is more active than SAPO-18 ➔ <u>HIGHER TOTAL ACIDITY AND ACID STRENGTH OF SAPO-34</u>**

Transformation of 1-butene

Deactivation by coke

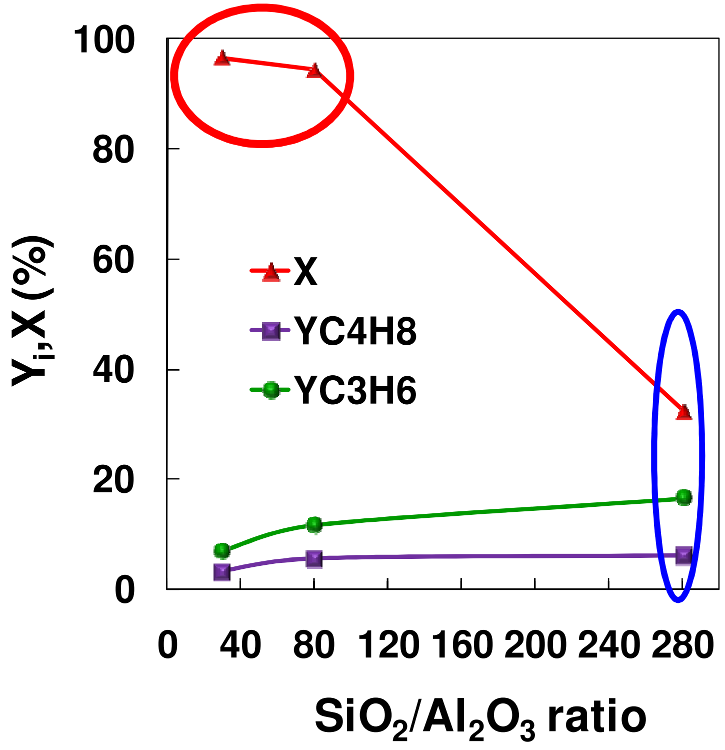
SAPO-34 (4.7 wt%)> SAPO-18 (3.3 wt%) >HZ-280 (2.7 wt%)

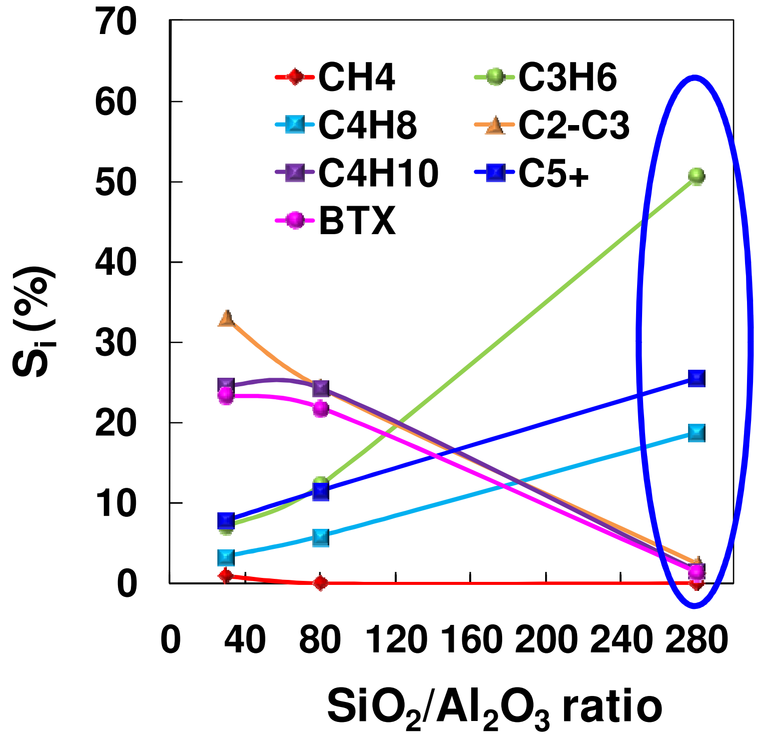




Transformation of ethylene

Effect of SiO_2/Al_2O_3 in HZM-5 zeolites



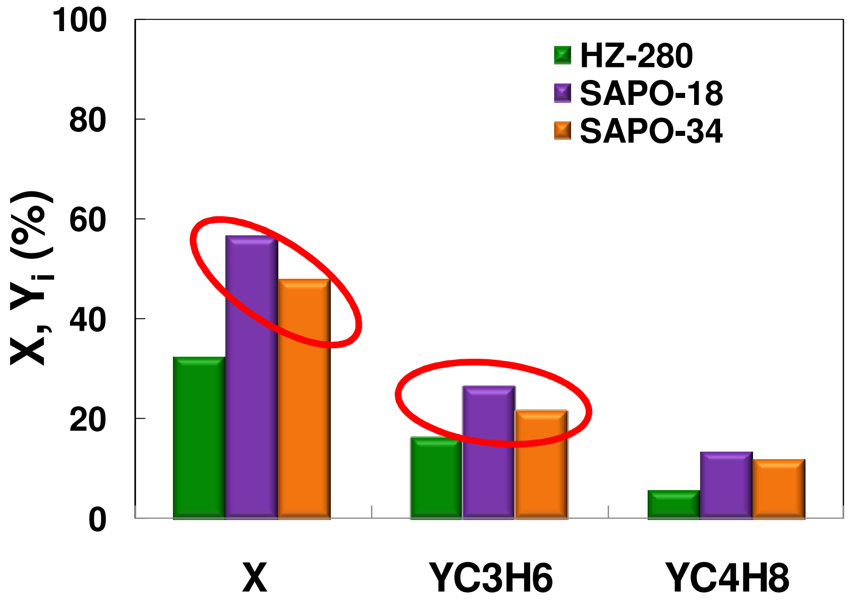


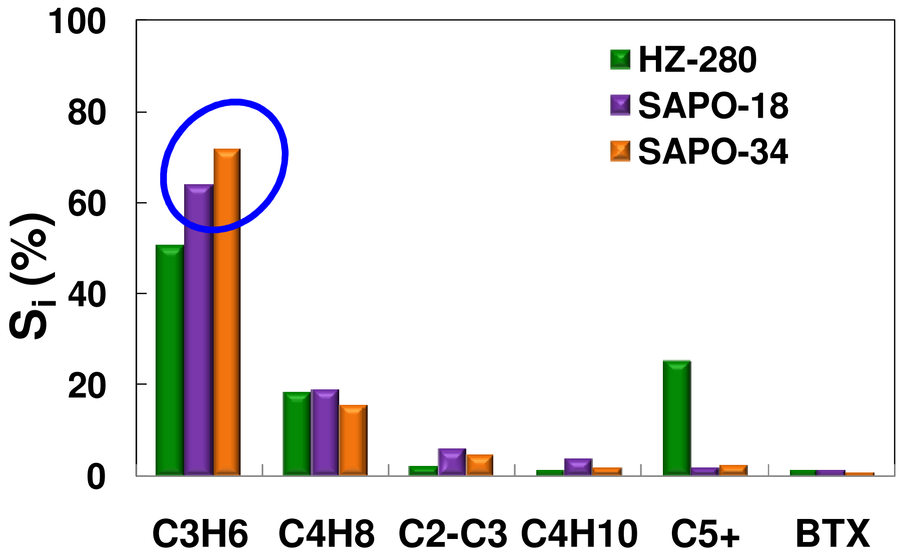
✓ Ethylene conversion requires low values of SiO_2/Al_2O_3 ratio

✓ HZ-280 ➔ SC_3H_6, YC_3H_6 ↑

Transformation of ethylene

Shape selectivity catalysts





- ✓ SAPO-34 and SA … ion and propylene …
- ✓ Steric res …
- ✓ Deactivatio …

SAPO-18 suitable for the selective production of propylene

INTRODUCTION
EXPERIMENTAL
RESULTS
CONCLUSIONS

CONCLUSIONS

- ✓ The moderation of total acidity and acid strength is an appropriate way to modify HZSM-5 zeolites in order to enhance propylene production
- ✓ SAPO-18 shows higher propylene selectivities using both feeds, although the deactivation by coke is slightly faster than for HZ-280 catalyst
- ✓ The use of SAPO-34 is conditioned by the fast deactivation by coke
- ✓ Operating conditions may have a great influence; the study should be extended to higher temperatures (up to 550 ºC) and feed composed of ethylene/propylene mixtures

ACKNOWLEDGMENTS

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E. Epelde is grateful for the Ph.D. grant from the Department of Education, University and Research of the Basque country (BFI08.122).

THANK YOU

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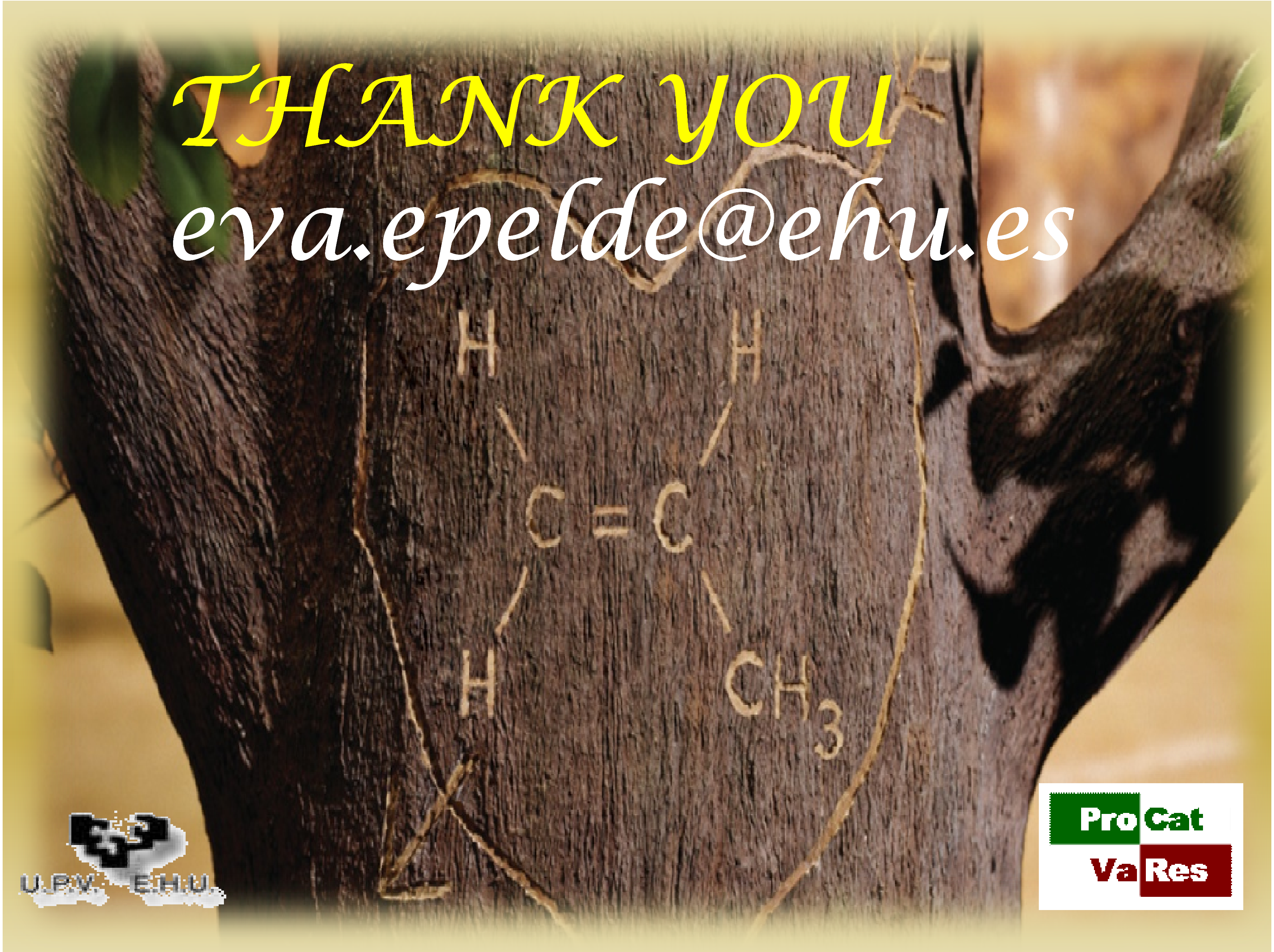

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