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

- Propylene worldwide 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

INTRODUCTION

RESULTS

CONCLUSIONS

2 % ‘On purpose’ technologies (paraffin dehydrogenation, metathesis)

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Catalytic Processes and Waste Valorization

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

**C₂-C₄ olefin interconversion**

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

**New catalyst development for C₂-C₄ 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 for propylene production from 1-butene and ethylene transformation.

Conversion - propylene yield, selectivity, stability

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**Catalyst preparation**

**Active phase** → **Wet extrusion, dry, calcination (550 °C, 2h)** → **Catalyst**

- Zeolite
  - HZSM-5 or SAPOs
- Bentonite (25 %)
- Alumina (30 %)
- **HZ-30 (SiO2/Al2O3=30)**
- **HZ-80 (SiO2/Al2O3=80)**
- **HZ-280 (SiO2/Al2O3=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

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**Catalyst characterization**

*N₂ adsorption-desorption (77 K)*

<table>
<thead>
<tr>
<th>Active phase</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( V_{\text{mesopore}} ) (cm³/g)</th>
<th>( V_{\text{micropore}} ) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ-30</td>
<td>448</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>HZ-80</td>
<td>556</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>HZ-280</td>
<td>512</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>SAPO-18</td>
<td>797</td>
<td>0.08</td>
<td>0.28</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>611</td>
<td>0.06</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( V_{\text{mesopore}} ) (cm³/g)</th>
<th>( V_{\text{micropore}} ) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ-30</td>
<td>202</td>
<td>0.53</td>
<td>0.042</td>
</tr>
<tr>
<td>HZ-80</td>
<td>209</td>
<td>0.48</td>
<td>0.036</td>
</tr>
<tr>
<td>HZ-280</td>
<td>231</td>
<td>0.38</td>
<td>0.048</td>
</tr>
<tr>
<td>SAPO-18</td>
<td>236</td>
<td>0.23</td>
<td>0.072</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>215</td>
<td>0.20</td>
<td>0.046</td>
</tr>
</tbody>
</table>
Catalyst characterization

DSC (150 °C)-
TPD of NH\textsubscript{3} (up to 550 °C)

<table>
<thead>
<tr>
<th>Active phase</th>
<th>Total acidity (mmol NH\textsubscript{3} g\textsuperscript{-1})</th>
<th>( T ) peak(°C) in the TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ-30</td>
<td>1.07</td>
<td>1st peak: 230, 2nd peak: 340</td>
</tr>
<tr>
<td>HZ-80</td>
<td>0.46</td>
<td>1st peak: 210, 2nd peak: 395</td>
</tr>
<tr>
<td>HZ-280</td>
<td>0.15</td>
<td>1st peak: 227, 2nd peak: 325</td>
</tr>
<tr>
<td>SAPO-18</td>
<td>0.37</td>
<td>1st peak: 243, 2nd peak: 335</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>0.64</td>
<td>1st peak: 258, 2nd peak: 348</td>
</tr>
</tbody>
</table>

These acid properties remain after agglomeration.
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

**EXPERIMENTAL**

**INTRODUCTION**

Reactor setup

**EXPERIMENTAL**

**RESULTS**

**CONCLUSIONS**

- Feed: 35 cm³ min⁻¹ of 1-butene or ethylene diluted (10%) in He
- 500 ºC
- Mass of catalyst: 0.55 g
- t = 5 h

Fixed bed reactor

Microactivity (316-L SS, Dᵢ = 9 mm)

- HPLC PUMP
  0.01 – 5 ml/min

- He 0-50 (ml min⁻¹)
- Air 0-50 (ml min⁻¹)
- Butene/Ethylene
- He purge (0-100 cm³ min⁻¹)

- HOT BOX
- BYPASS
- micro-GC AGILENT 3000
- MS5A PPQ Alumina OV1

- TEOM 1500 PULSE MASS ANALYZER
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

**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

Terms expressed as CH\(_2\) equivalent units, corresponding to zero time on stream

**EXPERIMENTAL RESULTS**

- **HZ-30 catalyst**
  - 500 °C, \( W/F_{A0} = 24.5 \) g catalyst h (mol CH\(_2\))\(^{-1} \)
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Transformation of 1-butene

Effect of SiO$_2$/Al$_2$O$_3$ in HZM-5 zeolites

- SiO$_2$/Al$_2$O$_3$ ratio
- Butene conversion
- C$_2$H$_4$ and C$_3$H$_6$ yield
- C$_2$H$_4$, C$_3$H$_6$ and C$_5+$ selectivities
- Hydrogen transfer reactions (catalyzed by strong acid sites)
- C$_2$-C$_4$ and BTX selectivities

HZ-280
Transformation of 1-butene

Shape selectivity catalysts

Severity of shape selectivity is higher for SAPOs (steric limitations) \( SC_3H_6 \uparrow \)

SAPO-34 is more active than SAPO-18 \( \Rightarrow \) HIGHER TOTAL ACIDITY AND ACID STRENGTH OF SAPO-34
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

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$_2$O$_3$ in HZM-5 zeolites**

- Ethylene conversion requires low values of SiO$_2$/Al$_2$O$_3$ ratio
- HZ-280 $\Rightarrow$ SC$_3$H$_6$, YC$_3$H$_6$
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

**Transformation of ethylene**

Shape selectivity catalysts

<table>
<thead>
<tr>
<th>Transformation</th>
<th>X, Y</th>
<th>C3H6</th>
<th>C4H8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>HZ-280</td>
<td>SAPO-18</td>
<td>SAPO-34</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**RESULTS**

- SAPO-34 and SAPO-18 suitable for the selective production of propylene
- Steric restrictions in SAPOs
- Deactivation rate: SAPO-34 >> SAPO-18
- SAPO-18 suitable for the selective production of propylene
Propylene production from 1-butene and ethylene catalytic cracking: Study of the performance of HZSM-5 zeolites and SAPOs

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 °C) and feed composed of ethylene/propylene mixtures.
This work was carried out with the financial support of the Ministry of Science and Innovation of the Spanish Government (Project CTQ2010-191888) and of the Department of Education Universities and Research of the Basque Government (Project GIC07/24-IT-220-07).

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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