Insights on bioethanol to hydrocarbons conversion over ZSM-5 zeolite by a transient technique

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Henry Ford, an automotive inventor told that ethyl alcohol was “the fuel of the future” in 1925.

In 1976, Meisel S.L.et.al. from Mobil discovered methanol conversion to hydrocarbons catalyzed by shape selective zeolites.
Sources of bio-ethanol are:

- First generation bioethanol - based on sugars and starch sources (feedstock consumable by humans).

- “Food Vs Fuel” debate resulted in Second generation bioethanol – produced from sustainable feedstock often termed as ‘advanced biofuels.’

- Third generation bioethanol derived from algae.
Introduction

WORLD FUEL ETHANOL PRODUCTION

- United states and Brazil contribute to 85% of world fuel ethanol production.
- There is an increased ethanol production from the past 3 decades.

ANNUAL U.S. FUEL ETHANOL PRODUCTION

- Ethanol usage is focused majorly as an:
  - Alternative source of fuel or
  - Towards value added chemicals.

Source: RFA analysis of public and private estimates
This research was focussed towards the production of value added chemicals from ethanol over a HZSM-5 zeolite.

Aim of the project is to understand the fundamentals of a reaction mechanism.

Three most debatable mechanisms in the literature were:
- Acid catalyzed
- Hydrocarbon pool involving aromatic surface species
- Radical assisted
Temporal analysis of products (TAP-3E) reactor was used in understanding the reaction mechanism.

- Operates under high vacuum $\approx 10^{-7}$ torr.
- Capable of pulse and continuous flow experiments.

- Typically 10 mg catalyst is used in thin zone configuration.
- Quadruple mass spectrometer with milli-second time scale resolution.
Materials and methods

- Two Kinds of pulse experiments:
  - Single-pulse experiments.
  - Pump-Probe experiments.

- Scan experiments: Temperature programmed desorption monitors the released surface species from the catalyst.

Materials

- HZSM-5 zeolite with Si/Al ratio’s of 15, 40 and 140 were used. The acid strengths of these zeolites were 0.75, 0.3 and 0.1 mol kg⁻¹ [1].

Ref:
Ethene conversion to higher hydrocarbons

Mole fractions as function of temperature (■: ethanol; □: diethyl ether; ●: ethylene; ○: C3+ hydrocarbons) \( W_{F_{EthOH}} = 8 \text{ kg}_{cat} \text{ s mol}^{-1}; p_{EthOH,0} = 10 \text{ kPa} \) [1]

Simulated ethanol conversion \( (X_{EthOH}) \) and butene yield \( (Y_{C4}) \) and corresponding simulated fractional surface coverages as a function of site time. \( (T=573 \text{ K}, p_{EthOH,0}=30 \text{ kPa}) \) [2]

Ref:
Ethene conversion to higher hydrocarbons

1st pulse

25th pulse

400th pulse
Ethene conversion to higher hydrocarbons

- Catalyst activity is restored by T.P.D. to 773 K.
- m/z = 78 (b) and 91 fragments representative of benzene and alkyl-substituted benzenes were the only detected fragments in T.P.D.

![Graph a) over fresh H-ZSM-5 (•, black), H-ZSM-5 after reaction and one TPD (•, blue), H-ZSM-5 after reaction two times and TPD (•, red), b) Intensity m/e=78 (benzene) during TPD after treatment of the catalyst with 400 pulses of ethene.](image)

- Butene has no $^{13}$C incorporation, while propene contains 5% $^{13}$C.
- After 50 pulses isotope exchange is completed.
Ethene conversion to higher hydrocarbons

- Route I (violet): dimerization of ethene to butene.

- Route II (green): formation of propene and butene via aliphatic surface intermediates.

- Route III (blue): formation of propene via aromatic surface intermediates.
Role of intermediates and products

Single - pulse experiments

- **Olefins**
  - Propene
  - 1-Butene
  - 1-Hexene
  - Diene
    - 1,4 - Hexadiene
  - Cyclodiene
    - 1,4 - Cyclohexadiene
- **Aromatics**
  - Benzene
  - Ethylbenzene
- **Olefins**
  - Conversion increased with C number.
  - Catalytic cracking pathways.
- **Aromatics**
  - Accumulated
Role of intermediates and products

Single-pulse experiments of 1-Butene

There is no hexene yield, which can be due to the complete catalytic cracking to smaller olefins in path I.

Propene yields from the first pulse, whereas pentenes formed after 50 pulses, as in path II.

Less pentene yield compared to the stoichiometric ratios comprise a tertiary cracking pathway of pentene to ethene and propene.

\[
\text{I} \quad 2\text{C}_4 \rightarrow \text{C}_8 \rightarrow \text{C}_2 + \text{C}_6 \\
\quad \quad 2\text{C}_3 \rightarrow \text{C}_6 \rightarrow \text{C}_2 + \text{C}_4 \\
\text{II} \quad 2\text{C}_4 \rightarrow \text{C}_8 \rightarrow \text{C}_3 + \text{C}_5 \\
\quad \quad \quad \text{C}_5 \rightarrow \text{C}_2 + \text{C}_3
\]
Role of intermediates and products

With olefins

C₂ + C₄ $\xrightarrow{\text{C}_6}$
C₆ $\xrightarrow{2\text{C}_3}$
C₂ + C₃ $\xrightarrow{\text{C}_5}$
C₃ + C₅ $\xrightarrow{\text{C}_8 \rightarrow 2\text{C}_4}$
2C₆ $\xrightarrow{\text{C}_{12} \rightarrow \text{C}_4 + \text{C}_8}$

With diene, cyclodiene and aromatics

H₂C=CH(CH₃) $\xrightarrow{\text{C}_2} \xrightarrow{\text{C}_8 \rightarrow 2\text{C}_4}$

C₃ $\xrightarrow{\text{C}_2}$

CH₃

CH₃

CH₃

CH₃
Role of intermediates and products

Catalyst coked under continuous flow experiments.

Temperature profile (top) and full scan of released hydrocarbons up to 200 a.m.u. (bottom) from the coked zeolite catalyst bed shown during 1500 scans.

Propene and butene undergoes scrambling with an average of 40 and 50% $^{12}$C incorporation.
Conclusions

✓ Hydrocarbon formation proceeds:

- Acid catalytic cracking via aliphatic surface species and
- side chain alkylation route via aromatic surface species.

✓ Dienes and cyclodienes are intermediates between aliphatic and aromatic surface species.

✓ Depending on the conditions, both aliphatic and aromatic surface species are involved in the hydrocarbon pool mechanism towards light olefin production.
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