"Ethylene oxychlorination catalysis: role of metal promoters on activity and selectivity of the process"

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Outlook

The chemistry of PVC and origin of Oxychlorination process

Influence of additives on base catalyst: multi technique approach

Summary & Conclusions

Ethylene Oxychlorination catalyst - state of art
Poly Vinyl-Chloride (PVC)

PVC industry is growing market with recycling efforts

Oxychlorination reaction \((\text{CuCl}_2) @ 230^\circ C\)
\[
\text{C}_2\text{H}_4 + 2\text{HCl} + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{H}_2\text{O}
\]

Direct chlorination \((\text{FeCl}_3)\)
\[
\text{C}_2\text{H}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2
\]

Cracking of 1,2-dichloroethane (EDC)
\[
\text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{CH}_2=\text{CHCl} + \text{HCl}
\]
The basic commercial catalyst is \( \text{CuCl}_2/\gamma-\text{Al}_2\text{O}_3 \)
Reaction mechanism

Chlorinated By-products

Promotes EDC degradation

2 CuCl

C₂H₄Cl₂

C₂H₄

CuCl responsible for Cu-migration

Hydrochlorolysis

Cu(II) Reduction

Cu(II) Oxidation

CuCl₂ responsible for particle agglomeration

Acid sites

2 CuCl₂

C₂H₄Cl₂

1/2 O₂

H₂O

2 HCl

Cu₂OCl₂

Promotes ethylene burn

Promotes over-chlorination

Chlorinated By-products

CuCl₂ responsible for particle agglomeration
Motivation & Challenges

- **Economic prospect:** Drive to decrease operation costs

- **Chemical & Environmental prospect:** selectivity could still be improved

- $\text{CuCl}_x$ is volatile and may be lost during reaction
  Hot spots, thermo–chemical side reactions

- Catalyst becomes sticky under certain reaction conditions (Fluid bed operation)

Adding dopants may solve the above problems
Our aim is very ambitious and can be summarized in the following four main points:

1) Influence on Surface and its properties
   Dispersion, active phase modification, acidity of the surface, etc.

2) Influence on reaction mechanism and kinetics

3) Influence on thermal & mechanical stability of the catalyst during reaction

4) Influence on Selectivity
Influence of Additives

Characterisation using combined spectroscopy

Kinetic tests

Activity & Selectivity

Doped Catalyst

Surface properties

Bulk and local environment

Reactants

In-situ mode or Operando mode

FTIR, UV-Vis and CO-chemisorption

EXAFS & XANES
Influence of Additives: On the Support

Modification on Surface acidity upon addition of dopant & chlorine

1) \[
\text{H-Cl} \quad \xrightarrow{\text{H-O}} \quad \text{H}_2\text{O} \\
\text{CuCl}_2 + \text{MCl}_x \\
\text{OH} \quad \text{Cl} \quad \text{OH} \\
\text{Al-O-Al} \quad \text{Al} \quad \text{Al} \\
\text{H-OH} \quad \text{OH} \quad \text{H} \\
\text{H2O} \\
\text{Unwanted species} \\
\]

2) \[
\text{CuCl}_2 + \text{MCl}_x \\
\text{OH} \quad \text{Cl} \quad \text{OH} \\
\text{Al-O-Al} \quad \text{Al} \quad \text{Al} \\
\text{H-OH} \quad \text{OH} \quad \text{H} \\
\text{H2O} \\
\text{Unwanted species} \\
\]

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Fourier Transform Infrared Spectroscopy

FTIR: a surface technique, basically give information about surface species

\[
\frac{I}{I_0} = \%T
\]

Peak position, intensity and width => Nature of species
Influence of Additives: The Surface

CO adsorbed FTIR

Lewis acid sites:

\[ \text{[= Al}^{3+} \text{]} \ldots \text{CO} \]

Brønsted acid sites

\[ \text{[= Al-OH]} \ldots \text{CO} \]

Evolution of the CO adsorbed FTIR spectra on the fresh catalyst activated @230°C under vacuum.

Influence of Additives: On the Surface
CO adsorbed FTIR

Catalyst: doped CuCl$_2$/γ-Al$_2$O$_3$

- Most of Lewis sites are compressed
- Strength of Brønsted sites follows the order:
  - La > Ca > Mg > Li > Cu > K > Cs

X-ray-Absorption Fine Structure

\[ \chi(k) = S_0^2 \sum_s N_s A_s \left( \frac{2k}{R_s} \right) e^{-\frac{2R_s}{\lambda}} e^{-2k^2 \sigma_s^2} \sin(2kR_s + \phi_s(k)) \]
Influence of Additives: On the Cu phase
Extended X-Ray Absorption Fine Spectroscopy

All dopants are competing with Cu to occupy alumina octahedral vacancy sites

La>Li>Mg>K>Cs>Cu

Evolution of the EXAFS spectra of the fresh catalyst activated @ 230°C

Influence of Additives: Kinetics

Byproduct formation follows the order

\[ \text{Cu}_{5.0} > \text{La}_{10.9}\text{Cu}_{5.0} > \text{Li}_{0.5}\text{Cu}_{5.0} > \text{Mg}_{1.9}\text{Cu}_{5.0} > \text{K}_{3.1}\text{Cu}_{5.0} \approx \text{Cs}_{10.4}\text{Cu}_{5.0} \]

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"It is evident that dopants had an influence on activity & in controlling the by-products"

Evolution of the products (by GC-MS) of the sieved catalyst interacted with reaction mixture @ 230°C - 350°C under steady state

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Summary & Conclusions

- Chlorine has significant influence on acidity of alumina surface.
- Dopant metals also influence the acidity of alumina especially in case of Lewis sites.
- Dopants increase the fraction of copper species on the surface.
- Dopants had a significant influence on activity and also in controlling the by-product formation compared to base catalyst $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$. 

Diagram:

- Acidity
- % Cu(II)
- Cu(II)/Cu(I)
- Activity & Selectivity
- Dopant
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Thanks for your Attention……...😊
Different Supports

Possible Supports:

- Zr-MOF (UIO-66) - An ultra stable Metal Organic Framework (MOF)
- Alumina modified with CeO$_2$.
- Mixed metal oxides: CeZrO$_x$, Mg$_{10}$Al$_7$O$_x$,
- Perovskite materials, Zeolite type materials.

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UIO-66: Commerically available Zr-MOF
CuCl$_2$ was loaded during synthesis of Zr-MOF (uio-66)
CuCl₂-Zr-MOF as redox catalyst - XANES

Ethylene+HCl+Air → Mass Spec

Conversion is very very low!!!

Cu wt% ≈ 1.2 %

Cu-MOF is showing red-ox properties...😊

CuCl₂ loaded onto Zr-MOF
CuCl$_2$-Zr-MOF as redox catalyst - XRD

CuMOF : CuCl$_2$ loaded onto Zr-MOF

CuMOF-@ RT and 160 C

Collapsing after interaction with reaction mixture....!!!

With reaction mixture
CuCl₂-Zr-MOF + gas. HCl - XRD

The structure started collapsing upon interaction with HCl at 120 °C.