Deactivation of Cu/SAPO-34 During Low-Temperature NH$_3$-SCR

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Introduction

zeolite deactivation

- low-temperature
  - NH$_3$ / H$_2$O inhibition
  - reversible

- high-temperature and H$_2$O
  - Breakdown of crystal lattice
  - irreversible

Small-pore zeolites less prone to HT collapse of lattice.

Is the Cu/SAPO-34 structure stable at low T?
Exposure to SCR conditions and water vapour

SAPO-34: hydrothermal synthesis

Aqueous ion exchange

Cu/SAPO-34 1.27 wt.% Cu

Cu/SAPO-34 2.60 wt.% Cu

Exposure to SCR conditions and water vapour

Degreening: 700 °C
3500 ml/min
400 ppm NH₃ / NO
5% H₂O (φ=16%)
8% O₂
T: 70-200 °C

Characterisation of Cu/SAPO-34 before (powder) and after (scraped off monolith) experiments
Experiments Performed in Order

- Ads 400ppm NH$_3$
- 400ppm NH$_3$, 400ppm NO, 8% O$_2$, 5% H$_2$O
- 400ppm NH$_3$, 400ppm NO, 8% O$_2$

- 70°C: 5% H$_2$O
- Other T: 400ppm NH$_3$, 400ppm NO, 8% O$_2$, 5% H$_2$O

- Ads 400ppm NH$_3$
- Ads 400ppm NH$_3$, 5% H$_2$O

... Characterisation
SCR over Cu/SAPO-34 (2.60 wt.%Cu)

**SCR+H$_2$O**

**SCR**
SCR over Cu/SAPO-34 (2.60 wt.%Cu)

Loss of activity: from 87 to 66%

No H₂O: Loss of activity smaller

Experiments Performed in Order

Ads 400ppm NH₃

400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O

400ppm NH₃, 400ppm NO, 8% O₂

70°C: 5% H₂O
Other T: 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O

Ads 400ppm NH₃

Ads 400ppm NH₃, 5% H₂O

... Characterisation
SCR over Cu/SAPO-34 (2.60 wt.%Cu)
Only water vapour at 70 °C
Experiments Performed in Order

- Ads 400ppm NH$_3$
- 400ppm NH$_3$, 400ppm NO, 8% O$_2$, 5% H$_2$O
- 400ppm NH$_3$, 400ppm NO, 8% O$_2$
- 70°C: 5% H$_2$O
  Other T: 400ppm NH$_3$, 400ppm NO, 8% O$_2$, 5% H$_2$O
- Ads 400ppm NH$_3$
- Ads 400ppm NH$_3$, 5% H$_2$O
- Characterisation
Loss of Activity Over Time
(2.60 wt.%Cu)

Experiments Performed in Order

- Ads 400ppm NH₃
- 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O
- 400ppm NH₃, 400ppm NO, 8% O₂
- 70°C: 5% H₂O
  Other T: 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O
- Ads 400ppm NH₃
- Ads 400ppm NH₃, 5% H₂O
- Characterisation
Loss of Crystallinity?

**XRD**

- 2.60 wt.% Cu, after
- 2.60 wt.% Cu, before
- 1.27 wt.% Cu, after
- 1.27 wt.% Cu, before

**BET**

- 544 m$^2$/g
- 473 m$^2$/g
- 582 m$^2$/g
- 420 m$^2$/g

Experiments Performed in Order

400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O

400ppm NH₃, 400ppm NO, 8% O₂

70°C: 5% H₂O
Other T: 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O

Ads 400ppm NH₃

Ads 400ppm NH₃, 5% H₂O

...
NH₃ Adsorption over Cu/SAPO-34 (2.60 wt.%Cu)

NH₃ storage identical after ca. 4.5h exposure to water vapour at 70 °C.
Hydrogen consumption decreased by 26 and 38\% (or less: up to 13\% binder in “after” samples) - small compared to loss of activity
Conclusions

• Synthesis of 1.27 wt.% Cu and 2.60 wt.% Cu Cu/SAPO-34
• 14 h enough for complete deactivation
• 600 °C treatment does not reverse deact.
• Plugging of pores and blocking of sites ruled out
• Breakage of crystal framework not dominating

→ transformation of copper sites
Acknowledgements

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