Selective Catalytic Reduction of NO_x with NH_3 over Cu-ZSM-5
– The Effect of Changing the Gas Composition

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Objective

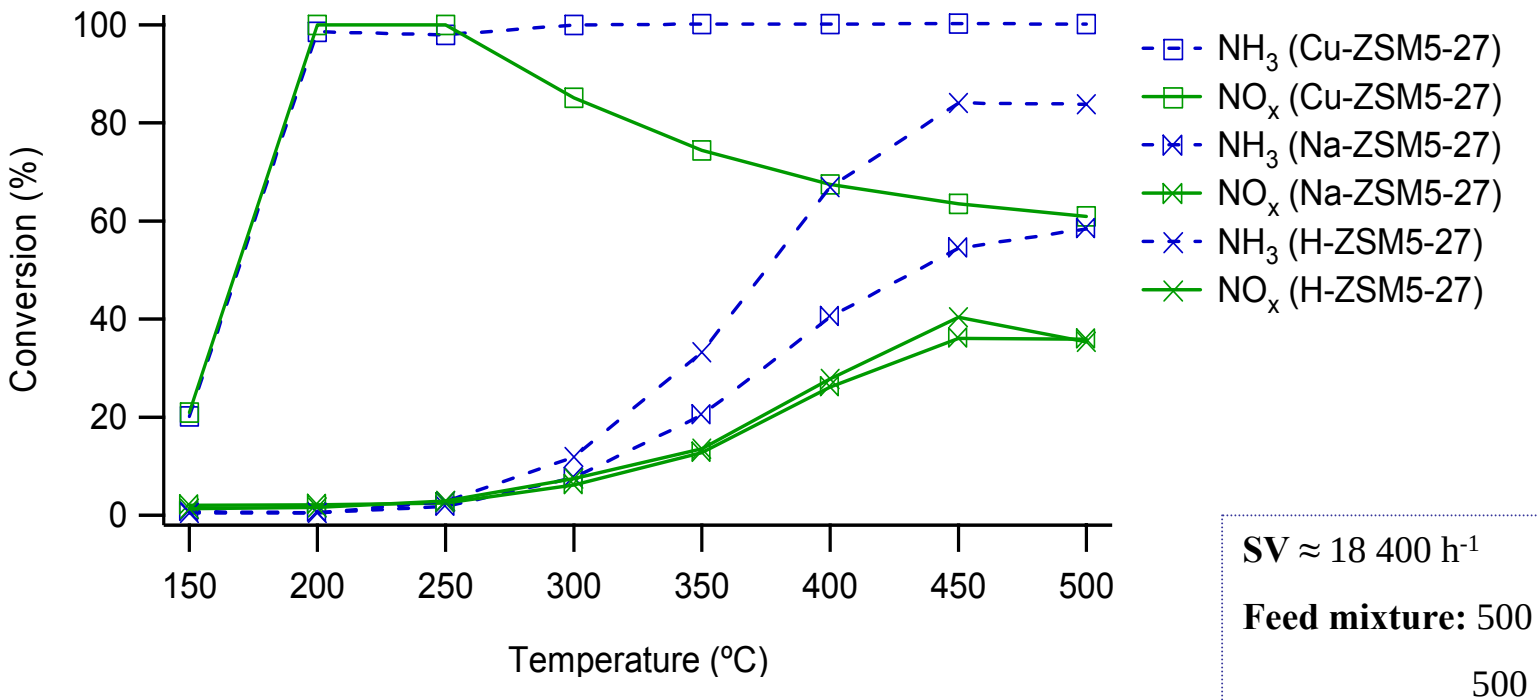
Evaluate NO_x reduction of Cu-ZSM-5 with ammonia as the reductant for the development of an automotive converter kinetic model.

Catalyst preparation

Zeolite powder	SiO_2/Al_2O_3	Primary crystal length (µm)	Copper ion exchange level (Cu/Al)
H-ZSM5-27	27	1-3	-
Na-ZSM5-27	27	1-3	-
Cu-ZSM5-27	27	1-3	0.35
Cu-ZSM5-55	55	3-5	0.27
Cu-ZSM5-300	300	<10	0.10

- Ion exchange from H^+ via Na^+ to Cu^{2+}
- **Catalysts coating:**
  - Monolith samples with ≈ 16.5 wt.-% washcoat
  - Washcoat composed of 80 % zeolite, 20 % binder (boehmite)

Effect of copper ion exchange



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO

500 ppm NH_3

8 % O_2

- Copper increases the overall activity
- Copper significantly increases the low temperature activity

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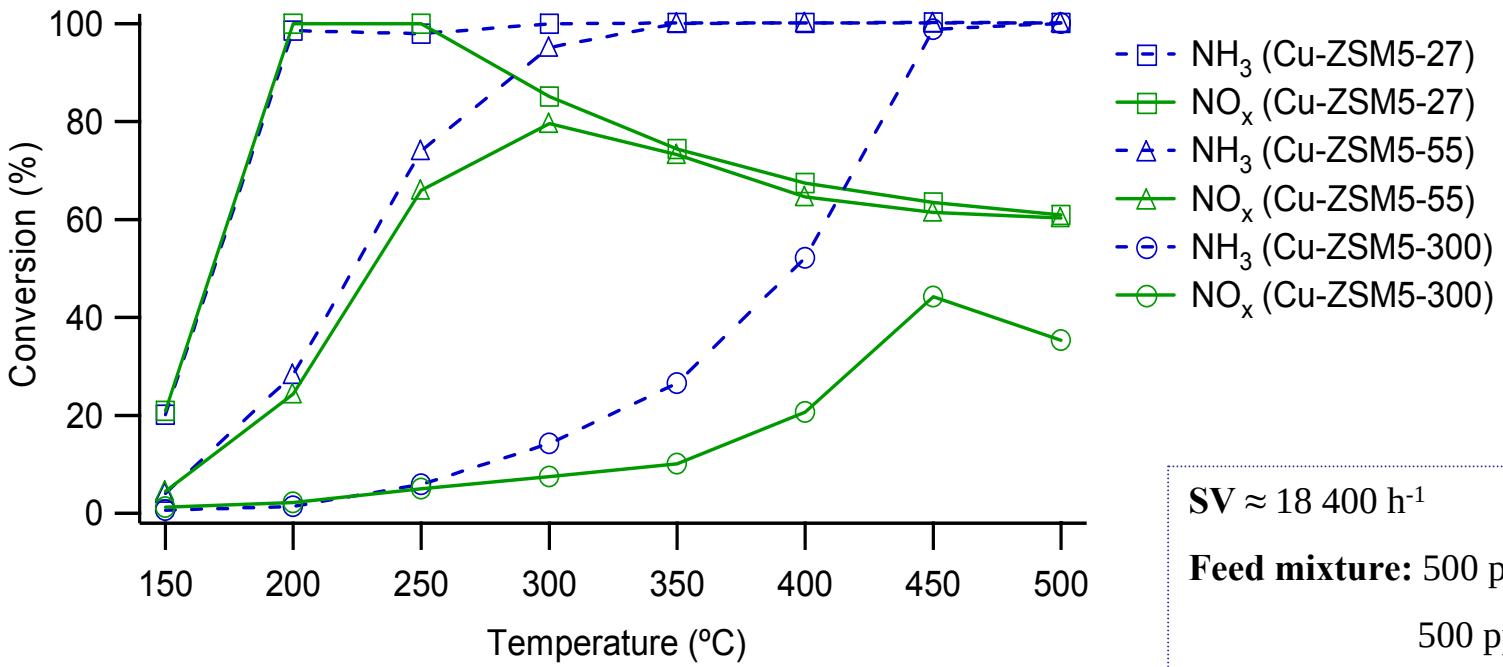
Effect of SiO_2/Al_2O_3 ratio



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO

500 ppm NH_3

8 % O_2

- Lower SiO_2/Al_2O_3 (27) has the highest NO conversion
- Lower SiO_2/Al_2O_3 ratios have the highest number of active sites

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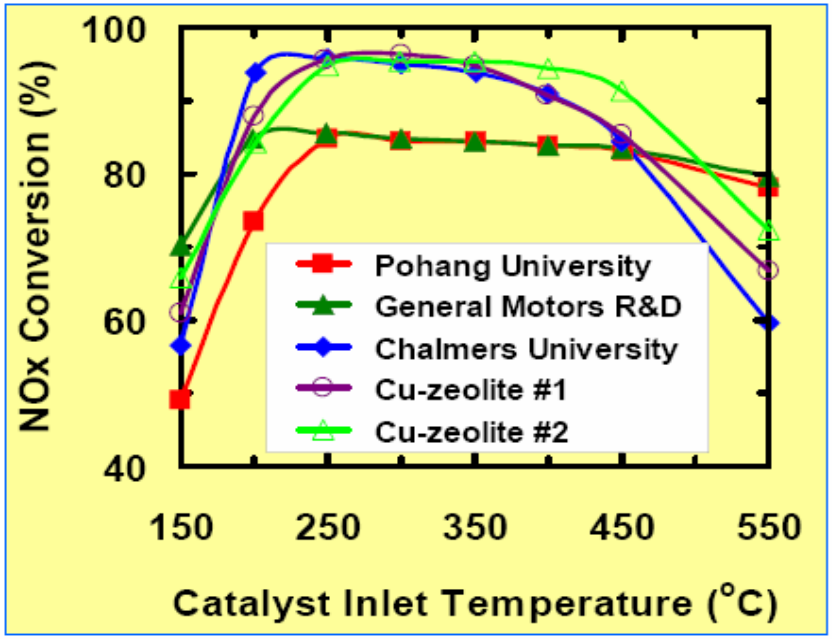
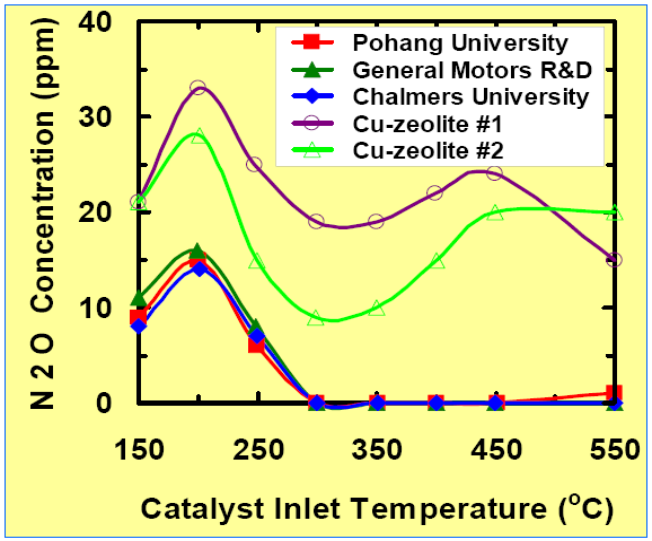
Comparison to supplier catalysts





Chalmers catalyst

→ Chalmers Cu-ZSM-5 catalyst shows similar activity as supplier Cu-zeolite catalysts and lower N_2O formation

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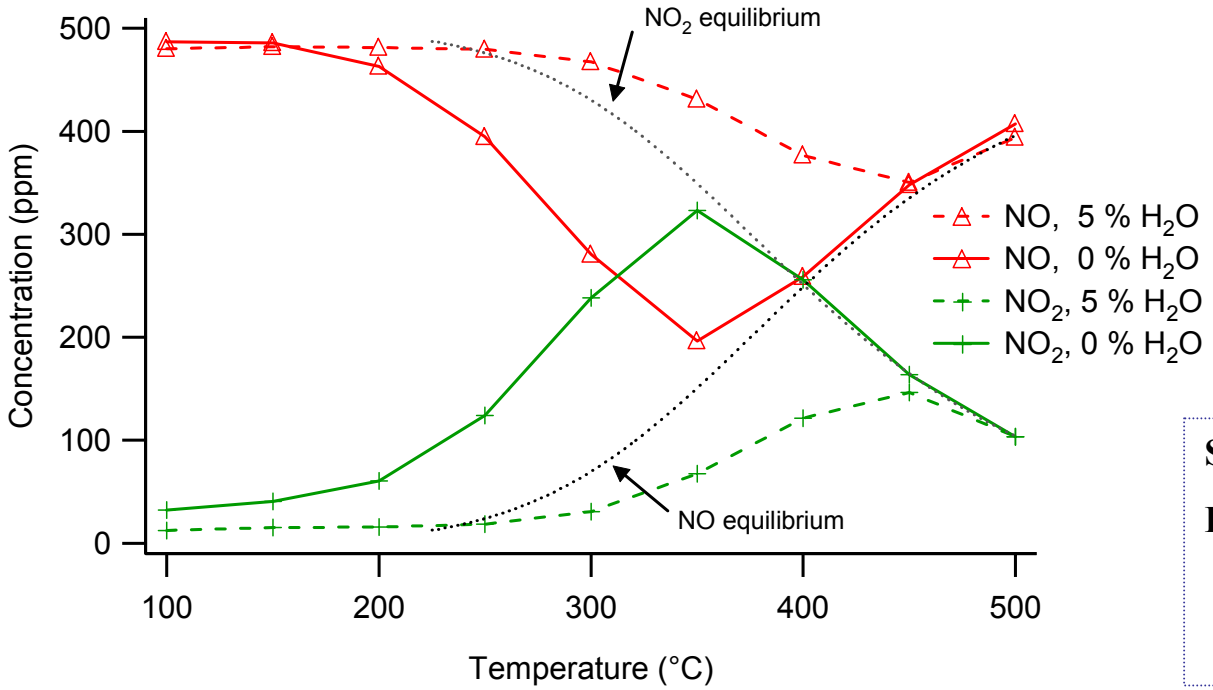
NO oxidation

- Effect of water



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO

8 % O_2

0 or 5 % H_2O

- NO oxidation important for SCR activity
- Water inhibits the oxidation rate

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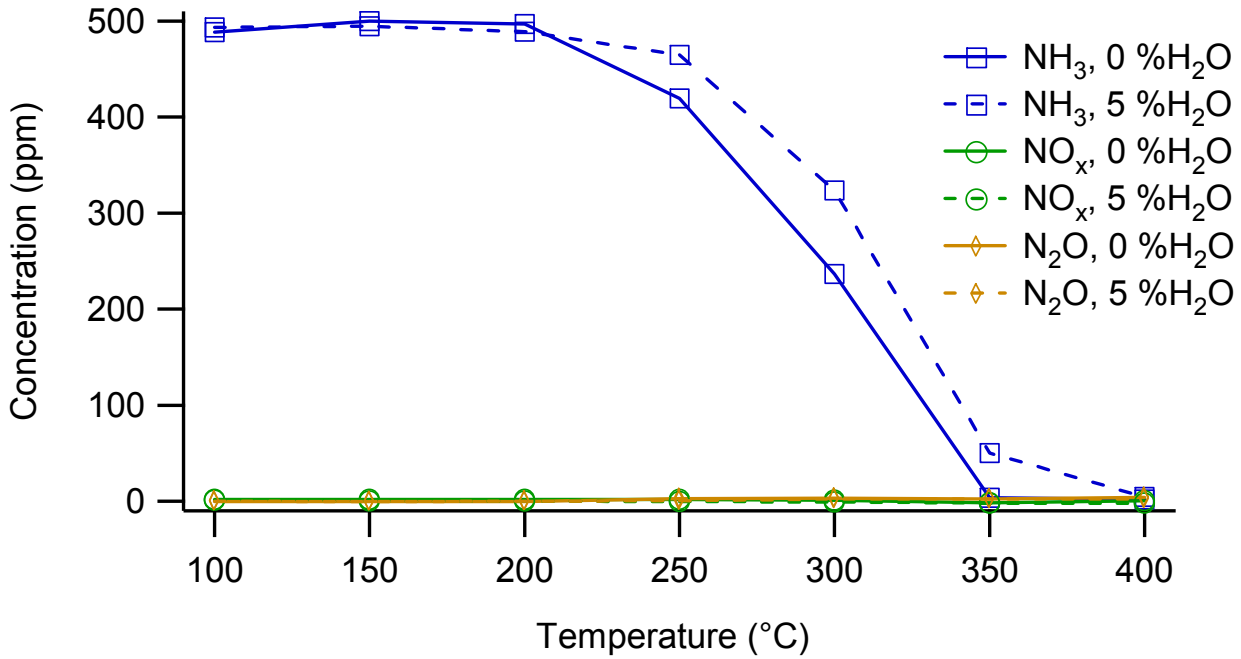
NH_3 oxidation

- Effect of water



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NH_3

8 % O_2

0 or 5 % H_2O

- NH_3 oxidation becomes important at high temperatures
- Water inhibits the oxidation rate

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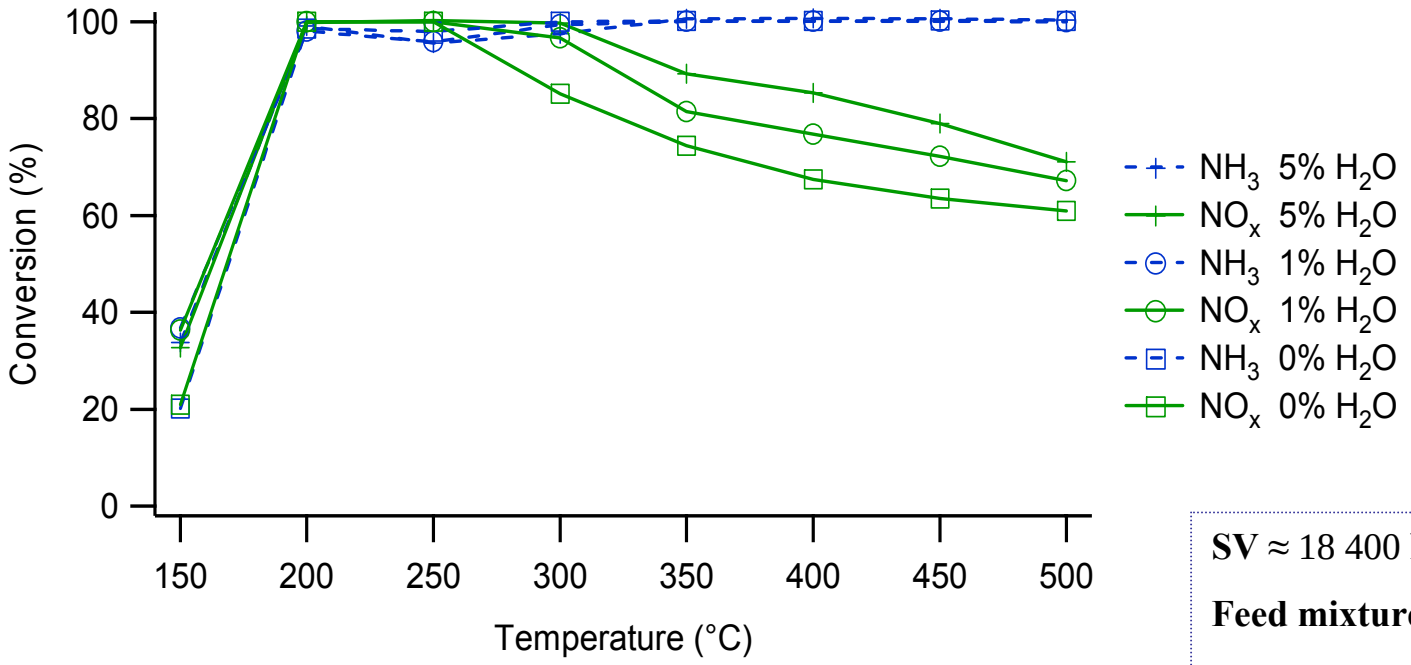
SCR activity and influence of H_2O



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO

500 ppm NH_3

8 % O_2

0, 1 or 5 % H_2O

- Water enhances the SCR activity at both high and low temperatures

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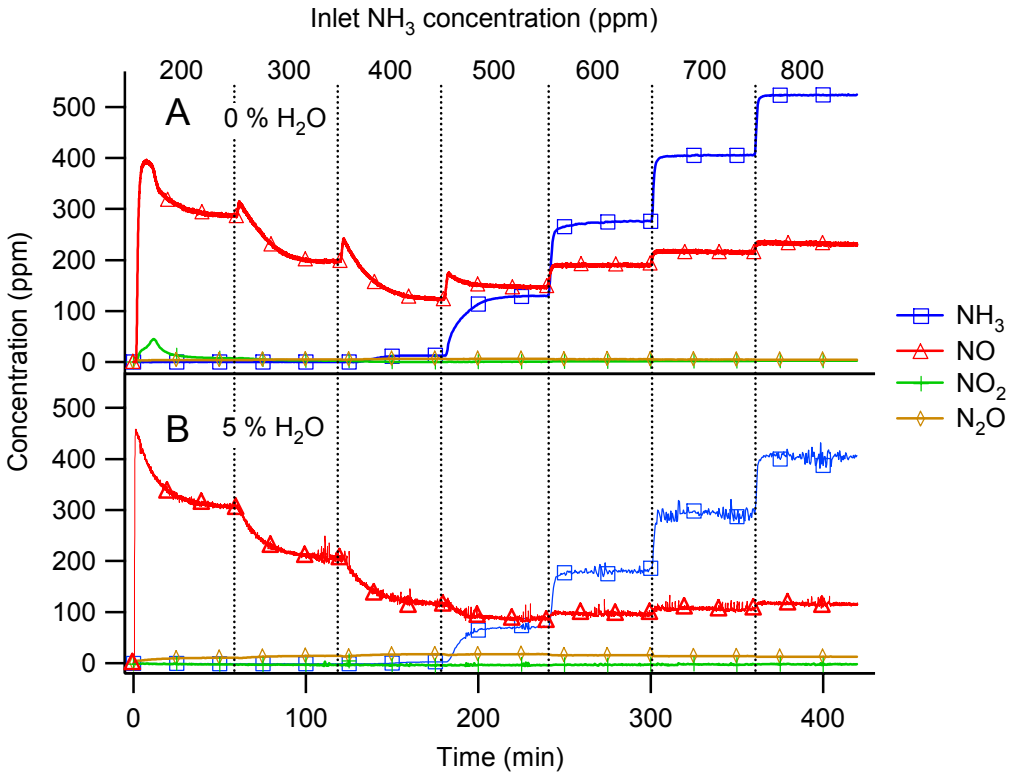
Effect of NH_3 concentration



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO

200-800 ppm NH_3

8 % O_2

0 or 5 % H_2O

Temperature: 175°C

- High ammonia concentrations limit the NO_x conversion
- Water suppresses the inhibition effect

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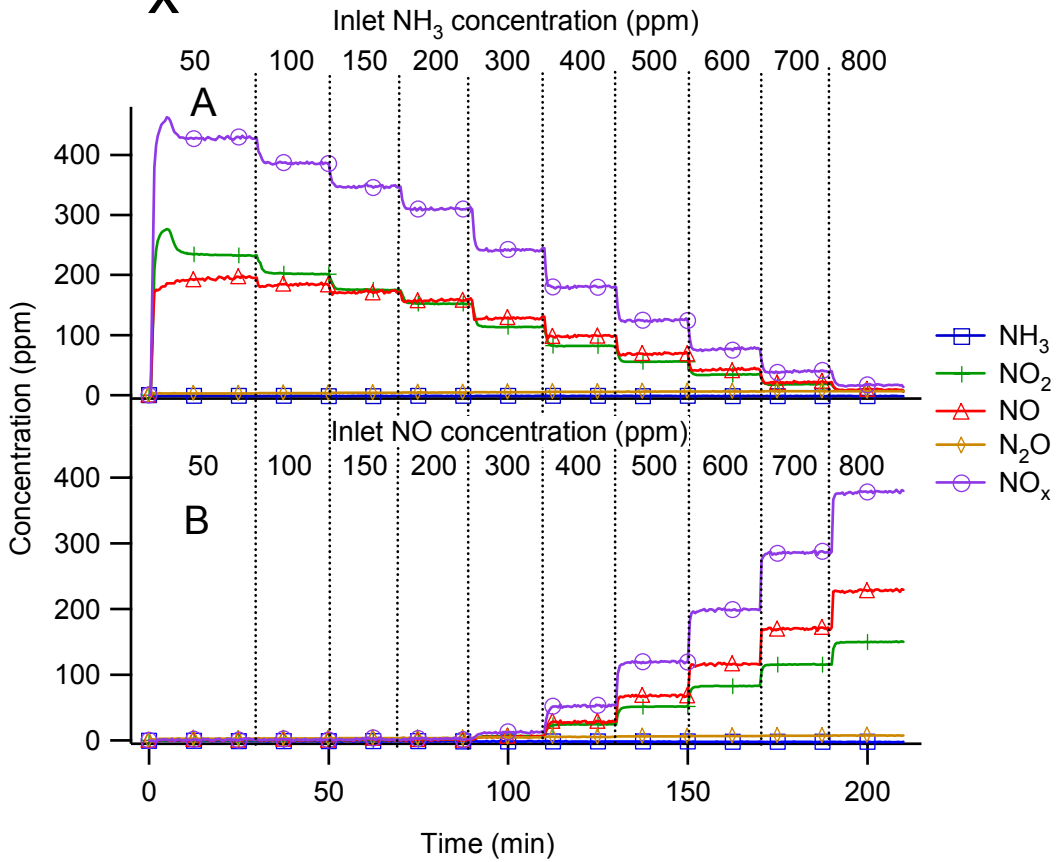
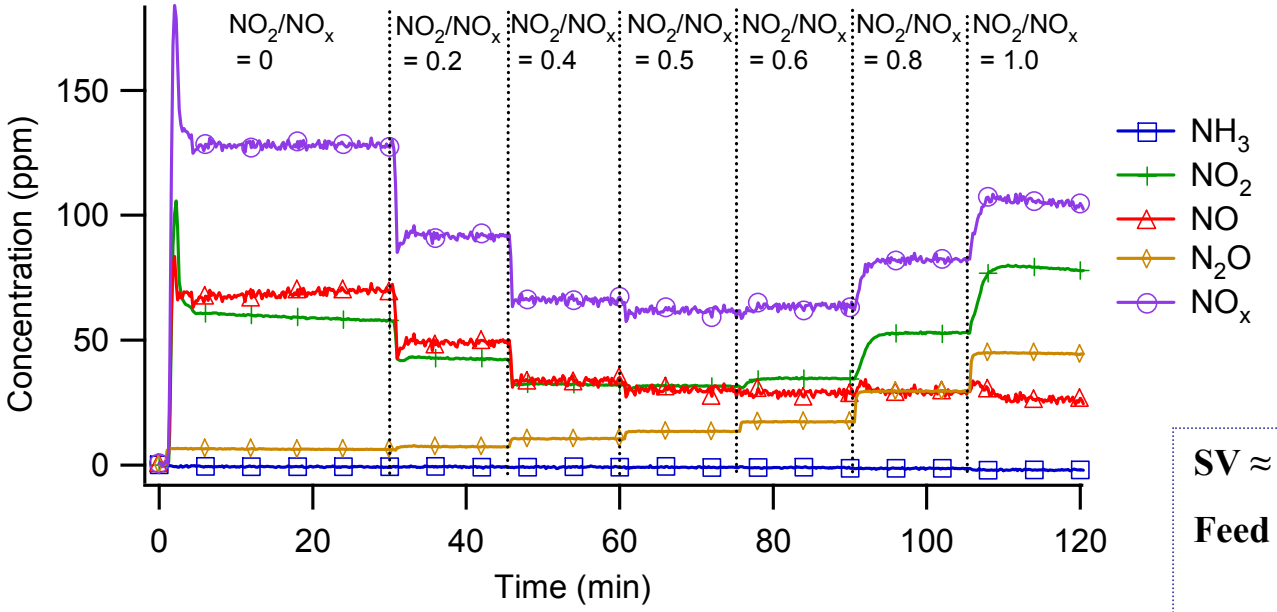
Effect of NO or NH_3 Concentration on NO_x Conversion at 350°C



- A: Increasing ammonia concentrations
- B: Increasing NO concentrations

Effect of NO/NO_2 ratio



SV ≈ 18 400 h^{-1}

Feed mixture: 500 ppm NO_x

500 ppm NH_3

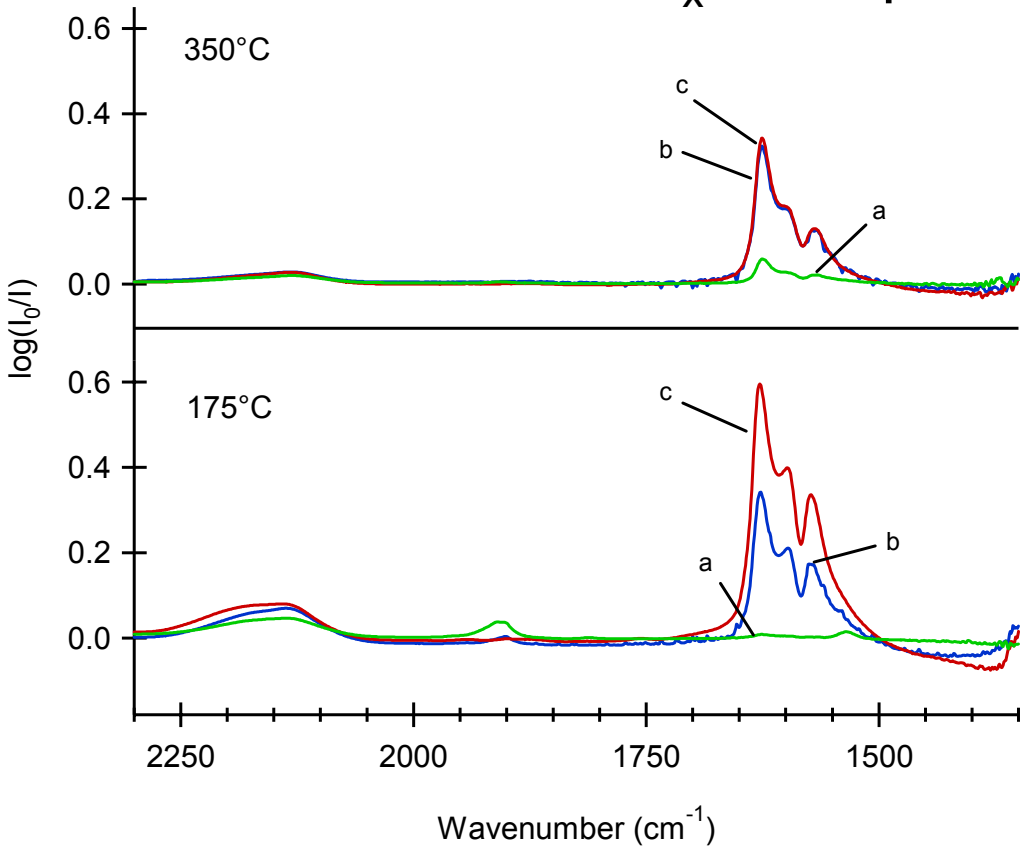
8 % O_2

Temperature: 350°C

- Highest conversion is at NO/NO_2=1
- N_2O formation increases with increasing NO/NO_2 ratios

FTIR spectra of species on Cu-ZSM-5

- NO_x adsorption



Feed mixture:

(a) 500 ppm NO

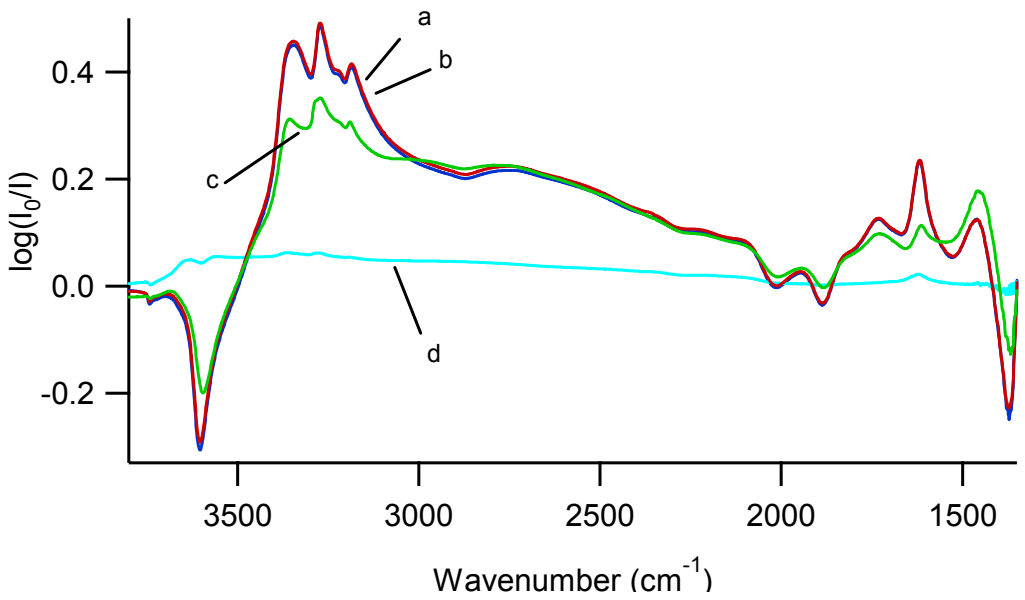
(b) 500 ppm NO and 8 % O_2

(c) 500 ppm NO_2

•The features between 1500 cm^{-1} and 1650 cm^{-1} can most likely be partially assigned to various nitrates

FTIR spectra of species on Cu-ZSM-5

- NH_3 adsorption



Feed mixture:

(a) 500 ppm NH_3 at 175ºC

(b) 500 ppm NH_3 and 8 % O_2 at 175ºC,

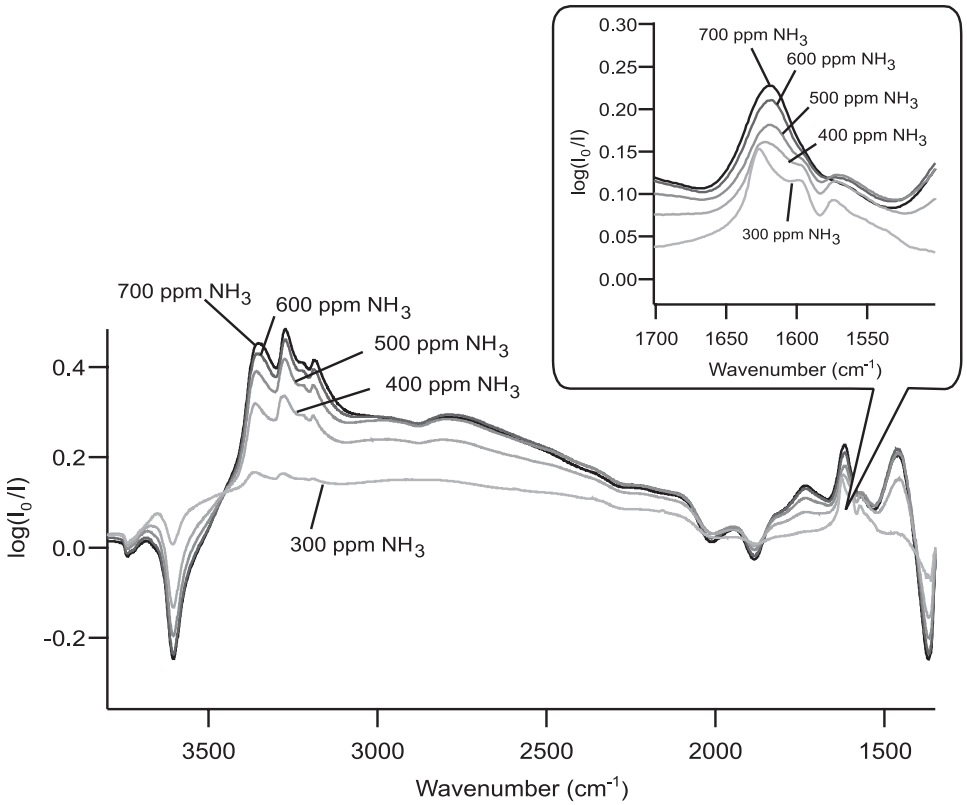
(c) 500 ppm NH_3 at 350ºC

(d) 500 ppm NH_3 and 8 % O_2 at 350ºC

- 1458 cm^{-1} can be assigned to NH_4^+
- 1620 cm^{-1} may be a combination of bands raised by both ammonia and water
- The broad feature in the 2200 – 3500 cm^{-1} has been assigned to water
- 3600 – 3610 cm^{-1} are assigned to OH vibrations at Brønsted acid sites

FTIR spectra of species on Cu-ZSM-5

- Adsorbed species during SCR conditions at 175°C



Feed mixture:
500 ppm NO, 8 % O_2 and
300 - 700 ppm NH_3

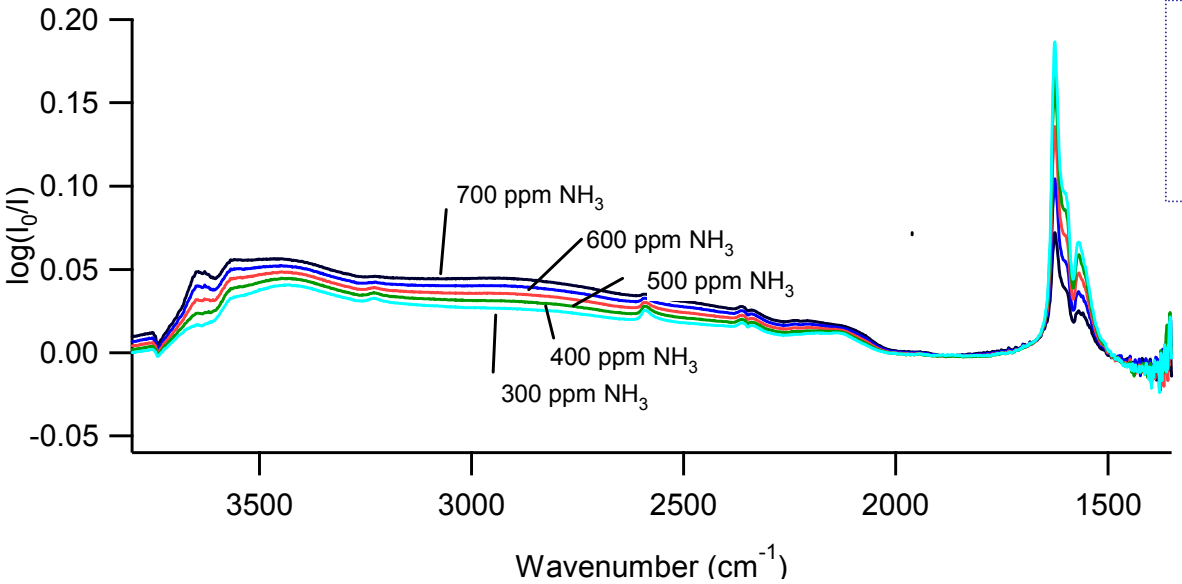
- 300 ppm NH_3, 500 ppm NO and 8% O_2: NH_3, NH_4^+ and NO_3^- on the surface
- NH_3 increases ⇒ adsorbed H_2O, NH_3 and NH_4^+ also increases

- High NH_3 conc.: adsorbed NH_3 increases, 2200 – 3500 cm^{-1} partly assigned to water cease to evolve, 1572 cm^{-1} reduces: nitrite/nitrate formation decreases

⇒ **NH_3 blocking effect**

FTIR spectra of species on Cu-ZSM-5

- Adsorbed species during SCR conditions at 350°C



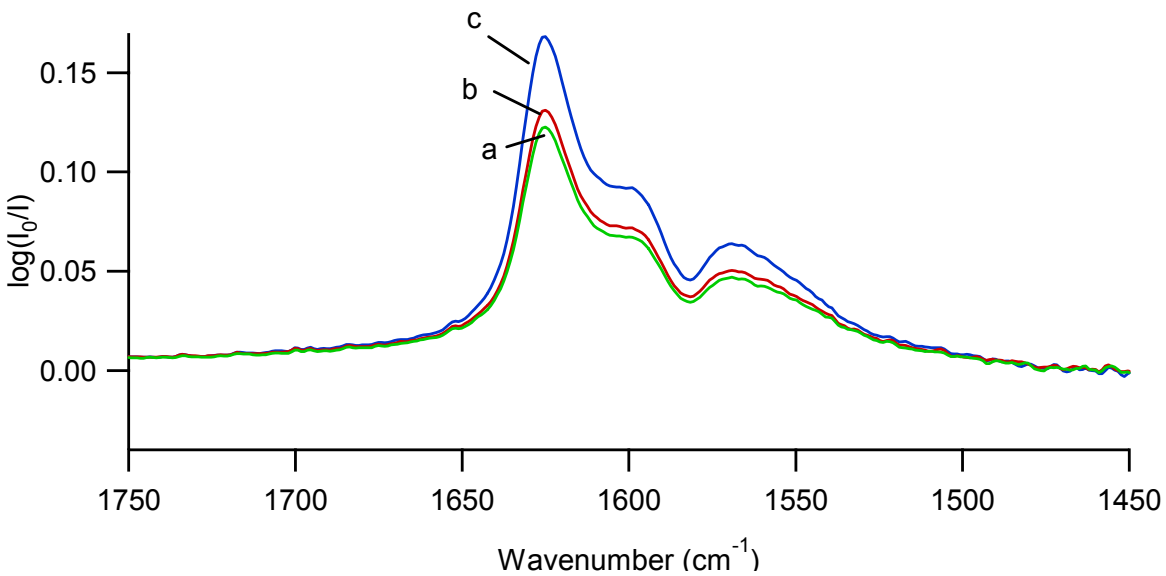
Feed mixture:

500 ppm NO, 8 % O_2 and
300 - 700 ppm NH_3

- No adsorbed ammonia on the surface, due to rapid NH_3 oxidation
- Nitrites/nitrates (1500 - 1650 cm^{-1}), water and possible OH groups on the surface
- NH_3 increases $\Rightarrow$ adsorbed H_2O increases and nitrite/nitrate decreases
- No NH_3 blocking effect

FTIR spectra of species on Cu-ZSM-5

- Influence of NO/NO_2 ratio



Feed mixture:

(a) 500 ppm NH_3, 8 % O_2, 500 ppm NO

(b) 500 ppm NH_3, 8 % O_2, 250 ppm NO, 250 ppm NO_2

(c) 500 ppm NH_3, 8 % O_2, 500 ppm NO_2

Temperature: 350°C

- The three spectra are similar.
- Increased nitrite/nitrate coverage is observed with an increased NO_2 fraction.

⇒ **The increased SCR activity with equimolecular amounts of NO and NO_2 can not be explained by surface species alone. It is possible that gas phase NO is needed in the SCR reaction.**

Summary (1)

- Zeolite effects
  - Ion-exchange with copper greatly enhances the NO_x reduction
  - NO_x conversion increases with decreasing SiO_2/Al_2O_3ratio.
  - Chalmers Cu-ZSM-5 catalyst shows similar activity as supplier Cu-zeolite catalysts and lower N_2O formation.
- Oxidation reactions
  - NH_3 oxidation is rapid at high temperature.
  - Oxidation of NO increases with temperature and reaches equilibrium at 350°C.
- Water effects
  - Enhanced NO_x reduction at both low and high temperatures.
  - Decreased NO and NH_3 oxidation.
- NO/NO_2 ratio
  - The highest NO_x conversion occurs when the concentration of NO equals NO_2.
  - N_2O formation increases when the NO_2/NO_x ratio increases.

Summary (2)

- Ammonia effects
  - At low temperature (175°C) high concentrations of ammonia blocks the NO_x reduction. The inhibition is suppressed by water.
  - A high ammonia concentration compared to NO concentration results in enhanced NO_x reduction at high temperature (350°C), where ammonia oxidation is rapid.

- FTIR spectroscopy
  - The adsorbed species on Cu-ZSM-5 was examined during exposure to NO, NO_2 or NH_3 and compared to the species during SCR conditions.
  - High NH_3 conc. at low temperature (175°C): reduces nitrite/nitrate formation $\Rightarrow$ NH_3 blocking effect.
  - High temperature (350°C) no ammonia on the surface and no NH_3 blocking, due to rapid NH_3 oxidation.
  - The increased SCR activity with equimolecular amounts of NO and NO_2 can not be explained by surface species alone. It is possible that gas phase NO is needed in the SCR reaction.