



DECOMPOSITION OF N₂O IN THE NITRIC ACID INDUSTRY:

**Definition of structure-activity relations as a tool to
develop new catalysts**

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Decomposition of N₂O in the nitric acid industry: Definition of structure-activity relations as a tool to develop new catalysts

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Introduction

The nitric acid industry is one of the major sources of the greenhouse gas N₂O, which is 310 times more effective than CO₂ in trapping heat in the atmosphere. One of the most promising techniques is direct decomposition of N₂O in the tail gases of nitric acid plants (1). The state-of-the-art catalysts are only active at temperatures above 400°C, which means that they can be used only in a limited number of plants. The aim of this research is to develop a catalyst that lowers the temperature for N₂O decomposition to below 350°C. This will increase the number of plants that can use the direct decomposition technique for N₂O removal and will improve the cost efficiency for plants with a higher temperature.

Many researchers have investigated iron-zeolites in recent years. They are active for N₂O decomposition, show a high stability in the tail gases of nitric acid plants and are promoted by the presence of NO_x in the tail gases (2,3). Noble metal catalysts for N₂O decomposition have been studied less thoroughly than iron zeolites. They show high N₂O decomposition activity in diluted N₂O streams, but are inhibited by the oxygen, water and NO_x present in nitric acid plant tail gases (4).

This paper defines relationships between the structure of iron-zeolite and noble metal catalysts and their activity for N₂O decomposition. Several parameters of preparation and post-modification were evaluated for their importance in the formation of active species. Based on the knowledge of the structure activity relations, novel catalysts were found with a higher activity for N₂O decomposition than the state-of-the-art catalysts.

Results

Iron zeolites prepared by wet ion exchange in air showed higher activity than catalysts prepared by sublimation of FeCl₃ (5), in spite of the fact that by wet ion exchange not all the charge compensation sites are occupied with iron ions and that iron oxide clusters are formed on the outer surface of the zeolite. The catalyst can be further improved by controlling the pH during the ion exchange, in order to keep the iron in the preferred oxidation state. An Fe-FER catalyst prepared at a stable pH of 2.5 showed higher N₂O conversion than the same catalyst for which the pH was not controlled during preparation.

Iron-zeolite catalysts have been characterized by TPR, FTIR, MAS-NMR and Mössbauer spectroscopy. It was found that tuning the pH prevented the formation of iron oxides to a significant extent. A relation was found between the occurrence of a Fe²⁺-species and the activity for N₂O decomposition. Figure 1 shows that the height of the Fe²⁺-NO peak at 1874 cm⁻¹ in an *in situ* DRIFT NO-adsorption experiment on Fe-BEA catalysts correlates with the activity for N₂O decomposition (6). Mössbauer spectroscopy confirmed the existence of Fe²⁺ species in the most active catalysts. Figure 1 also shows that pre-treatment of the catalyst in an inert gas improves N₂O decomposition.

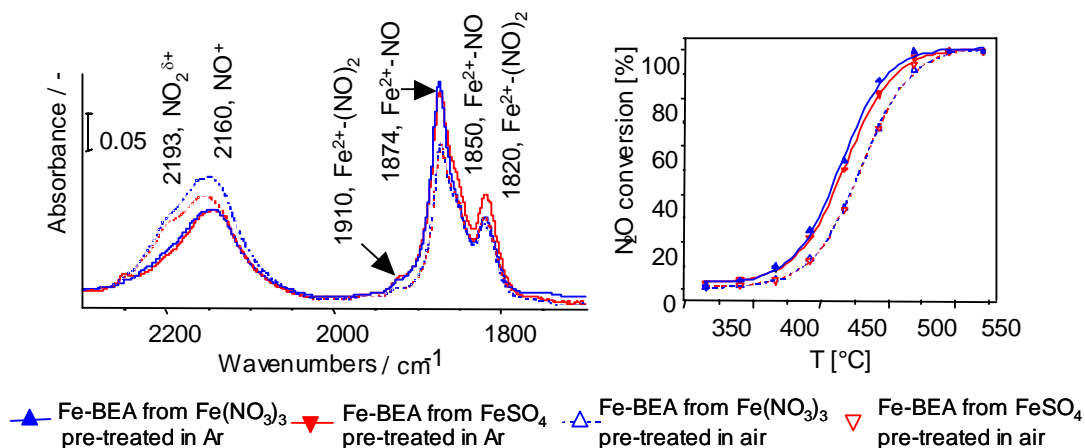


Figure 1: Left: DRIFT spectra of NO adsorbed on various Fe-BEA catalysts at 50 °C in flowing 5% NO/He. Right: N₂O decomposition activity vs. Conditions: 1500 ppmv N₂O in He, $W/F_{N_2O} = 8.65 \cdot 10^5 \text{ g.s.mol}^{-1}$, $p = 4 \text{ bar(a)}$.

Figure 2 shows that with both a Co-Rh-zeolite and an Fe-zeolite high N₂O conversions are reached at temperatures around 350 °C. Interestingly, N₂O conversion on the Co-Rh-MOR catalyst did not improve when pressure was increased from atmospheric to 4 bar(a) (with unchanged W/F). For Fe-FER, on the other hand, the N₂O conversion curve was shifted to lower temperatures at 4 bar(a).

Both catalysts were stable for over 500 hours time-on-stream in simulated nitric acid plant off gas.

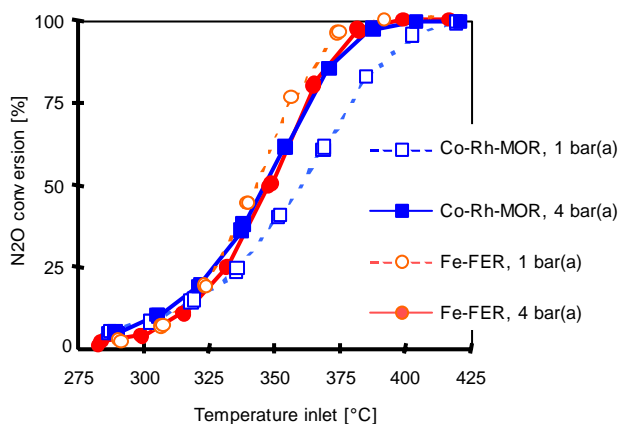


Figure 2: Conditions: 1500 ppmv N₂O, 200 ppmv NO, 0.5% H₂O, 2.5% O₂, $p = 4 \text{ bar(a)}$, $W/F_{N_2O} = 30 \text{ g.s.mol}^{-1}$

Conclusions

By unraveling the structure-activity relations, novel, more active catalysts were developed for the direct decomposition of N₂O. This reduces the emission of greenhouse gases.

References

- (1) J. Pérez-Ramírez, F. Kapteijn, K. Schöffel and J.A. Moulijn, *Appl. Catal. B* 44 (2003) 117
- (2) J. Pérez-Ramírez, F. Kapteijn, G. Mul and J.A. Moulijn, *Appl. Catal. B* 35 (2002) 227
- (3) M. Kögel, B.M. Abu-Zied, M. Schwefel, T. Turek, *Catal. Commun.* 2 (2001) 273
- (4) Y. Li and J.N. Armor, *Appl. Catal. B* 1 (1992) L21
- (5) J.A.Z. Pieterse, S. Booneveld and R.W. van den Brink, submitted to *Appl. Catal. B*
- (7) G. Mul, J. Pérez-Ramírez, F. Kapteijn and J.A. Moulijn, *Cat. Lett.* 80 (2002) 129

Decomposition of N₂O in the nitric acid industry:

Definition of structure-activity relations as a tool to develop new catalysts

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Catalytic Emission Reduction

ECN Clean Fossil Fuels

Energy Research Center of the Netherlands



Nitrous oxide is a potent greenhouse gas

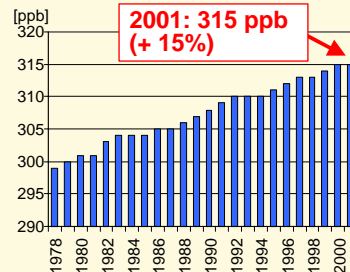
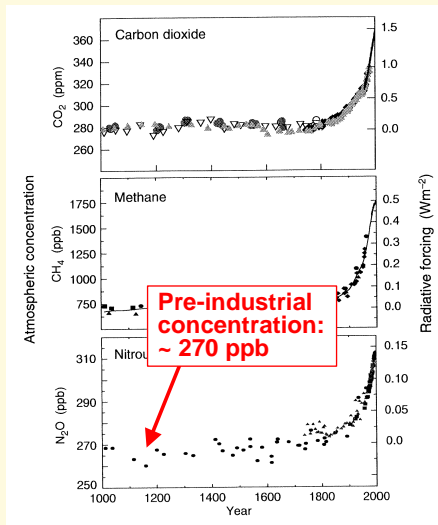
'N₂O is 310 times as effective in trapping heat in the atmosphere than CO₂ over a 100-year time period'



	GWP
CO ₂	1
CH ₄	21
N₂O	310
HFC-23	11.700



N₂O concentrations in the atmosphere are rising...



Earth trends 2002 World Resources Institute

Nitrous oxide is a potent greenhouse gas



The chemical industry is an important source of N₂O

Industrial Sources

- Nylon production (adipic acid)
- Fertiliser production (HNO₃)

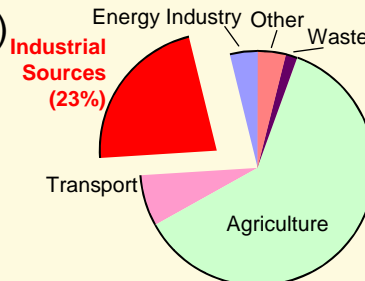
Agriculture

- Fertiliser use
- Leguminous crops

Transport

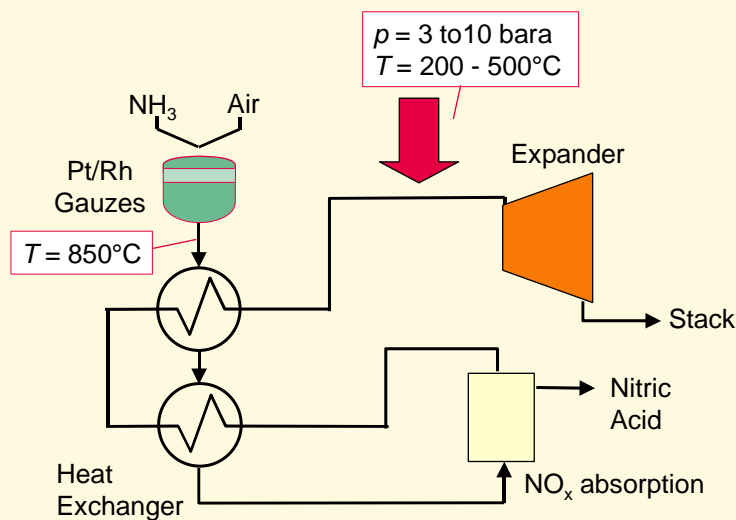
- Three-way catalyst
- Diesel Engines

N₂O sources in the EU, 1998



European Environmental agency, 1999

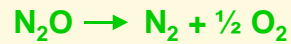
N₂O removal in a nitric acid plant



Tail Gas :

1500 ppm N₂O
 200 ppm NO_x
 2.5% O₂
 0.5% H₂O

Direct decomposition of N₂O



Catalysts:

- Zeolite supported iron catalysts
 - Fe-ZSM-5 active > 400°C
 - N₂O conversion promoted by NO
- Zeolite supported (promoted) noble metal catalysts
 - Shown to be very active in pure N₂O

Iron Zeolites

Noble metals



Direct decomposition of N₂O



Goals

- N₂O removal at 350°C under nitric acid plant tail gas conditions
- Stability of the catalyst
- Costs < 1€/ ton CO₂-equivalents removed

Means

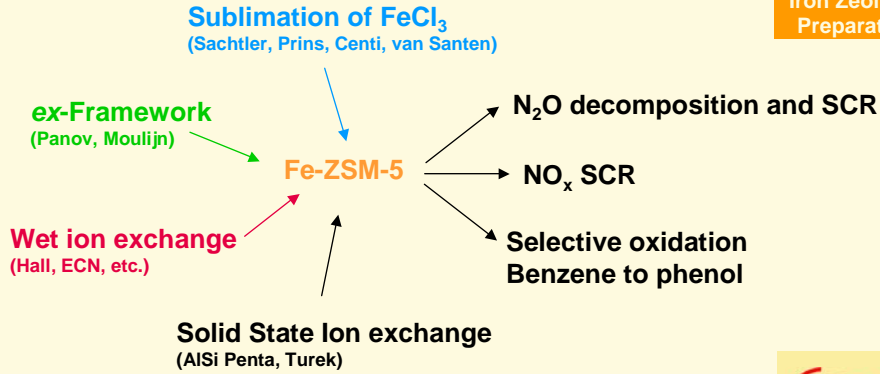
- Structure-activity relation to aid catalyst optimisation



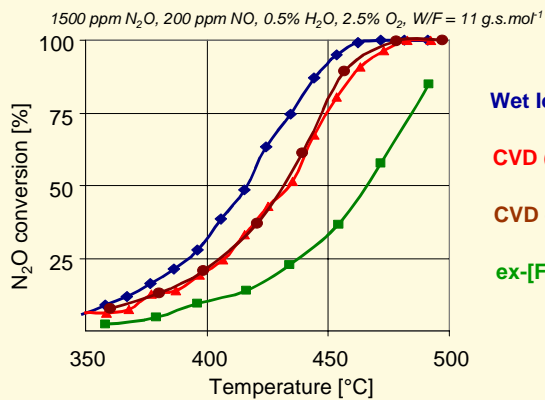
Different ways to prepare Fe-zeolite catalysts



Iron Zeolites:
Preparation



Fe-ZSM-5: Influence of preparation method



Wet Ion Exchange

CVD (TU/e)*

CVD (ECN)

ex-[Fe,Al]-ZSM-5**

	Si/Al	Fe wt%	Fe/Al
Wet Ion Exchange	11.5	2.3	0.37 [#]
CVD (TU/e)*	19.4	3.6	0.97
CVD (ECN)	11.5	2.6	0.45
ex-[Fe,Al]-ZSM-5**	31.5	0.7	0.15

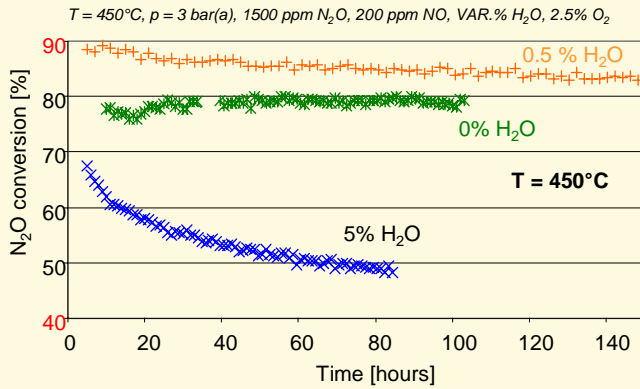
[#] 50% is inactive Fe_2O_3

➤ Wet ion exchange in air yields active catalysts

Pieterse, Booneveld, van den Brink, App. Cat. B 51 (2004) 215
* Zhu, Hensen, Mojet, van Wolput, van Santen, Chem. Commun. (2002) 123
** Pérez-Ramírez, Mul, Kapteijn, Moulijn, Chem. Commun (2001) 693.

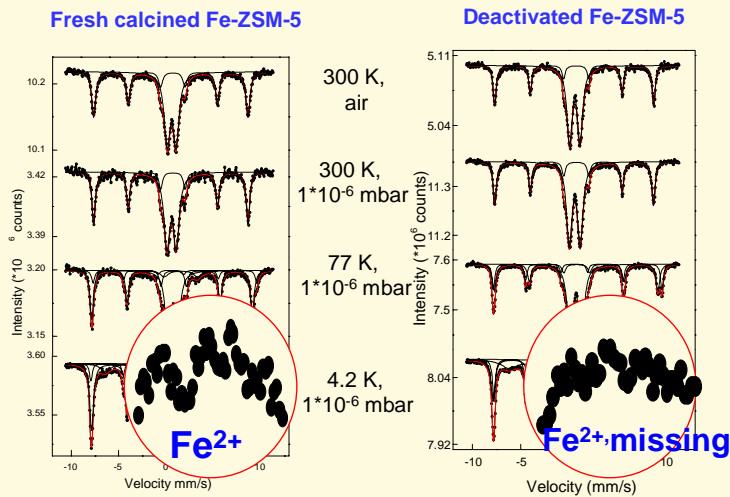


Deactivation Fe-ZSM-5

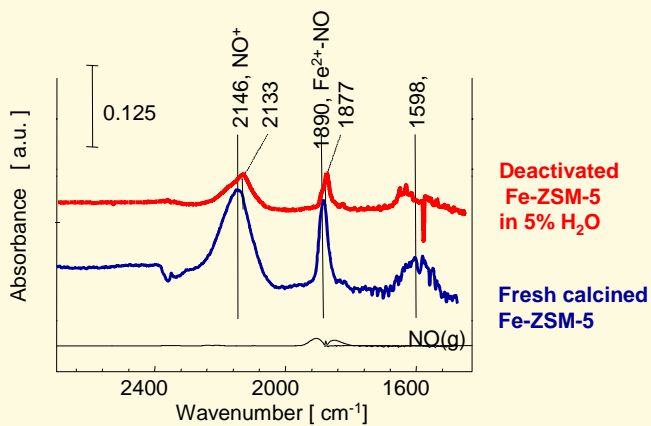


- Fe-ZSM-5 prepared by WIE deactivates
- Deactivation caused by steam

Mössbauer spectroscopy: Fe^{2+} species disappear



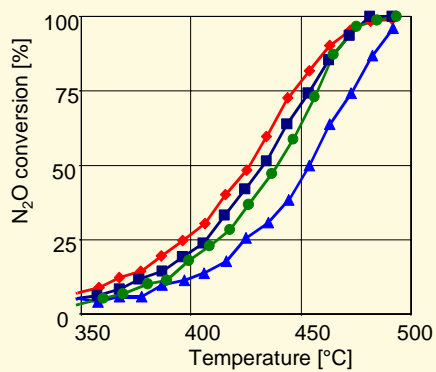
FTIR of adsorbed NO: NO-peaks on Fe²⁺ are decreased



- De-activated catalyst has less Fe²⁺
- Is this a clue to the active species ?

Different zeolites: Fe-FER and Fe-BEA also very active

1500 ppm N₂O, 200 ppm NO, 0.5% H₂O, 2.5% O₂, W/F = 11 g.s.mol⁻¹

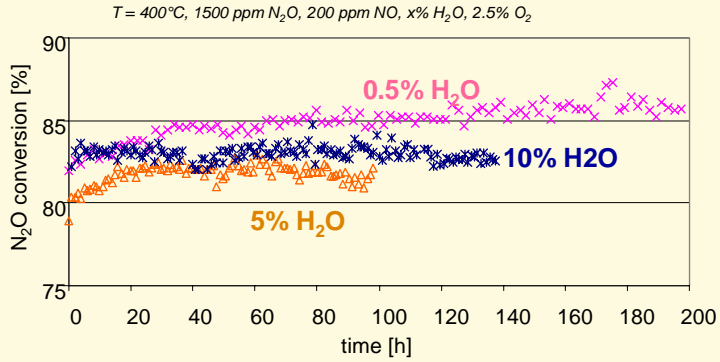


- Fe-FER and Fe-BEA comparable to Fe-ZSM-5

Stability Fe-BEA catalyst: no deactivation at 10% H₂O



Iron Zeolites



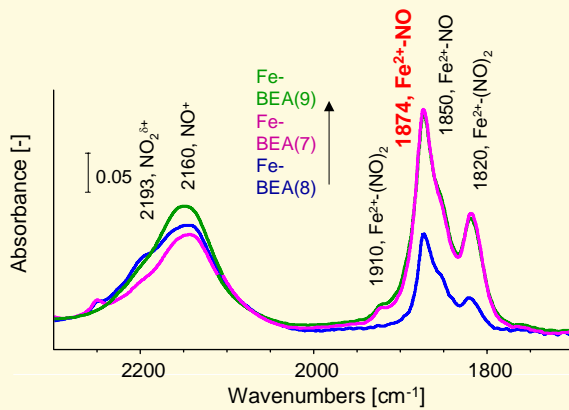
➤ Fe-BEA shows no deactivation in 10% H₂O



FTIR of adsorbed NO on Fe-BEA



Iron Zeolites



➤ Only Fe²⁺ sites react with nitrogen oxide

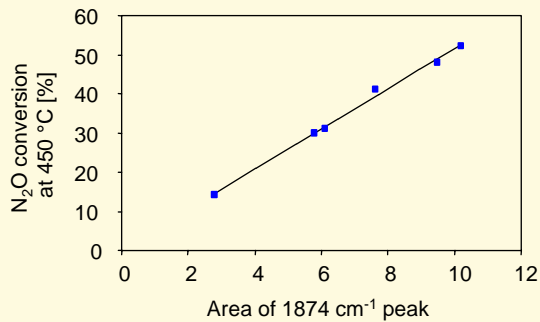
Mul, Pérez-Ramírez, Kapteijn, Moulijn, Cat.Lett. 80 (2002) 129



FTIR of adsorbed NO: correlation between activity and Fe²⁺-NO



Iron Zeolites



- IR vibration at 1874 cm⁻¹ correlates with activity
- NO on Fe²⁺ is the active site ?

Mul, Pérez-Ramírez, Kapteijn, Moulijn, Cat.Lett. 80 (2002) 129

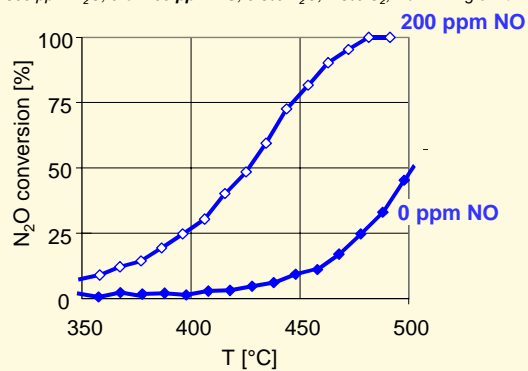


Fe-FER with or without NO in the feed



Iron Zeolites

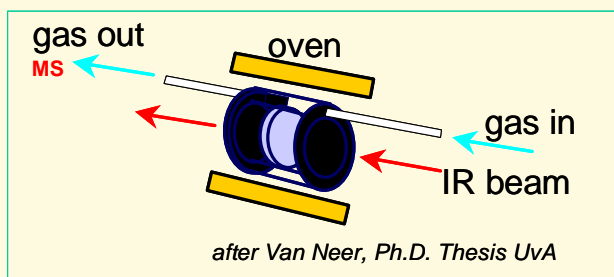
1500 ppm N₂O, 0 or 200 ppm NO, 0.5% H₂O, 2.5% O₂, W/F = 11 g.s.mol⁻¹



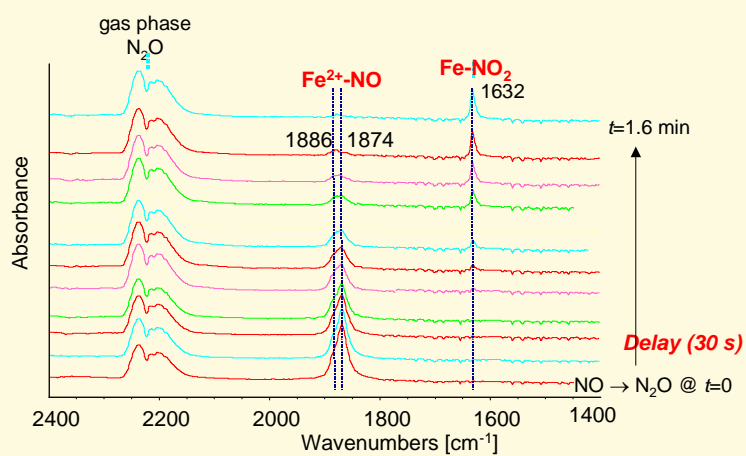
- Nitrogen oxide has a large promoting effect



In-situ FTIR experiments



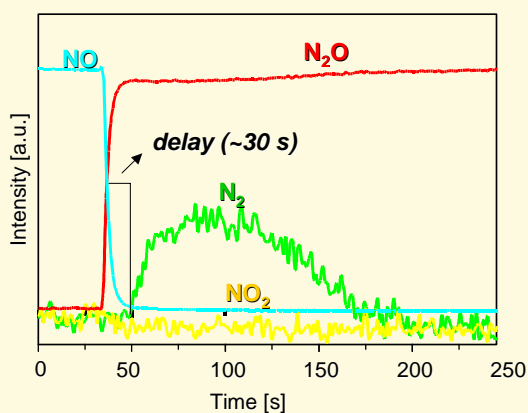
In situ FTIR - switch NO to N₂O at 350 °C



- adsorbed NO oxidised to adsorbed NO₂
- No nitrate formation !

Mul, Pérez-Ramírez, Kapteijn, Moulijn, Cat.Lett. 77 (2001) 7

MS signal - switch N₂O to NO at 350°C

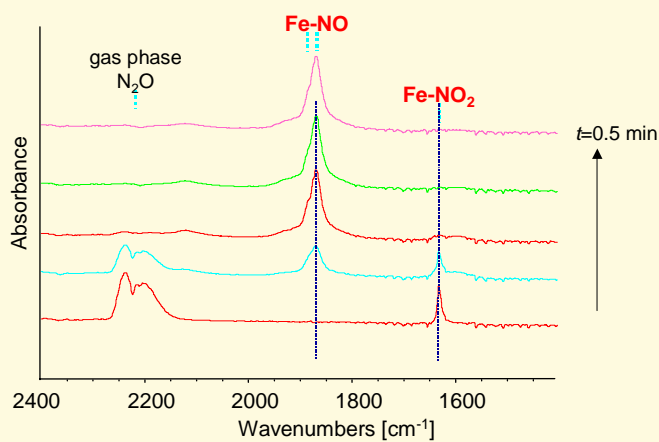


Iron Zeolites:
NO effect

➤ Same delay in N₂ evolution as in adsorbed NO₂ formation

Mul, Pérez-Ramírez, Kapteijn, Moulijn, *Cat.Lett.* 77 (2001) 7

In situ FTIR - switch N₂O to NO at 350 °C

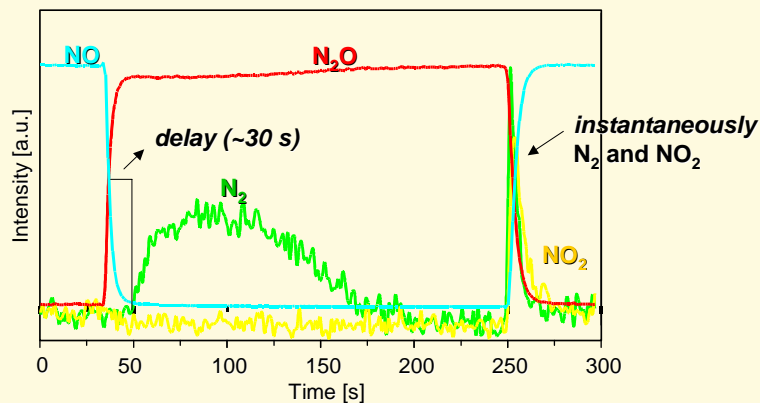


Iron Zeolites:
NO effect

➤ NO displaces NO₂ rapidly

Mul, Pérez-Ramírez, Kapteijn, Moulijn, *Cat.Lett.* 77 (2001) 7

MS signal - switch N₂O to NO at 350 °C

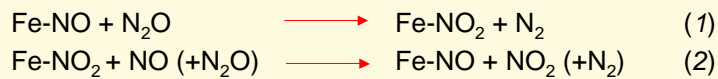


Iron Zeolites

Mul, Pérez-Ramírez, Kapteijn, Moulijn, Cat.Lett. 77 (2001) 7



In-situ IR observations



Iron Zeolites

- Process (1) is delayed : Requires NO to desorb, creating free sites for N₂O activation
- Delay time decreases with increasing temperature
- NO₂ slowly desorbs
- NO displaces NO₂



Fe²⁺ species involved in N₂O conversion

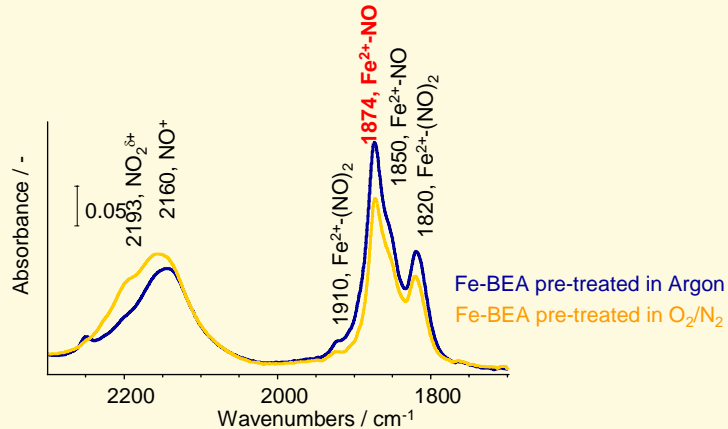


- The presence of specific Fe²⁺ species is essential in the N₂O decomposition.
 - Nature of active site not known
- How to increase number of Fe²⁺ species?
 - Pre-treatment
 - During preparation

Iron Zeolites



(Auto)reduction instead of calcination of Fe-BEA



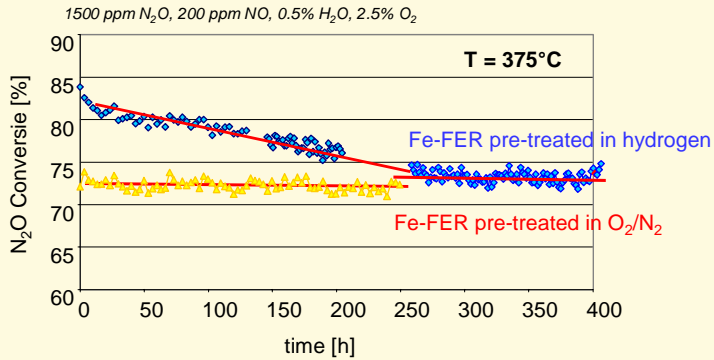
Iron Zeolites

- Peak at 1874 cm⁻¹ increases
- Higher activity for N₂O decomposition?



Reduction instead of calcination of Fe-FER

TU Delft



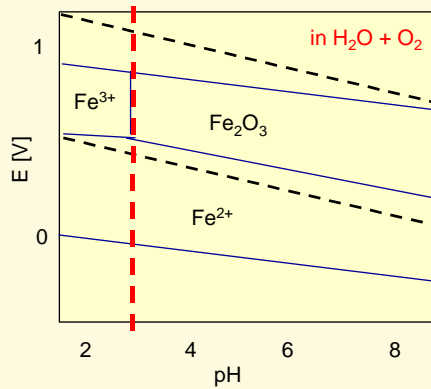
Iron Zeolites

- Initial activity of reduced catalyst is higher
- Slow convergence to activity of calcined sample

ECN

Preparation of Fe-zeolites Chemistry of iron ions in solutions

TU Delft



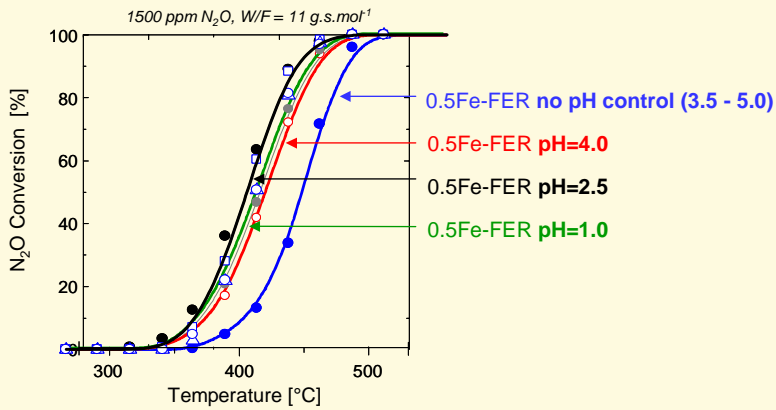
Iron Zeolites

- pH below approx. 3: no precipitation
- Exclusion of oxygen has no effect on activity

Pourbaix and De Zoubov, in: Pourbaix, M, Atlas of Electrochemical Equilibria in Aqueous Solutions, 1966. Flynn, Chem. Rev. 84 (1984) 31

ECN

Preparation of FER at controlled pH

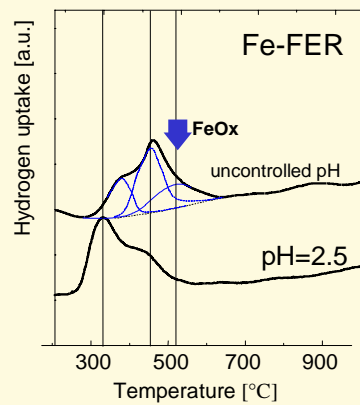


Iron Zeolites

- N₂O decomposition highest for pH = 2.5
- N₂O decomposition decreases at lower pH



TPR spectrum of Fe-FER: more iron reduction at low temperature

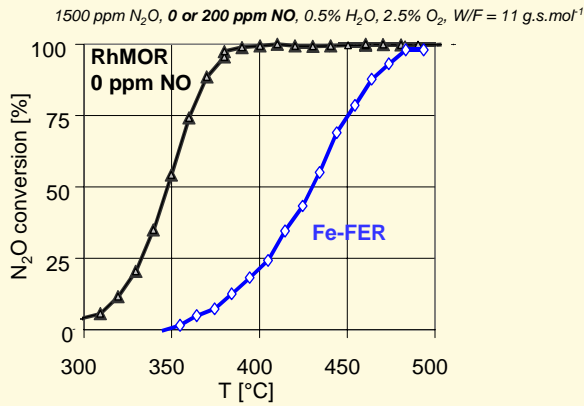


Iron Zeolites

- Low-temperature reduction peak is high



Rh-MOR with and without NO in the feed

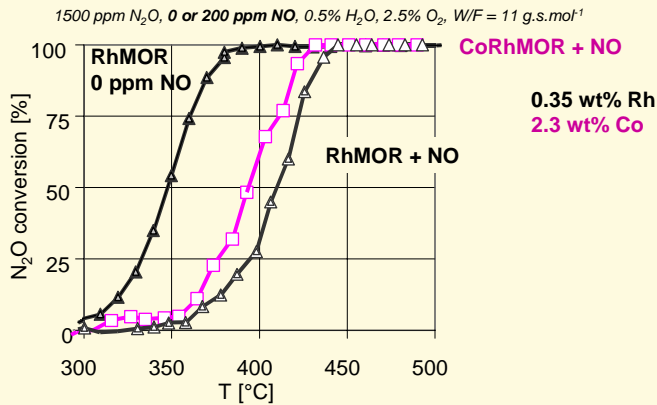


TU Delft

Noble metals



Rh-MOR with and without NO in the feed



TU Delft

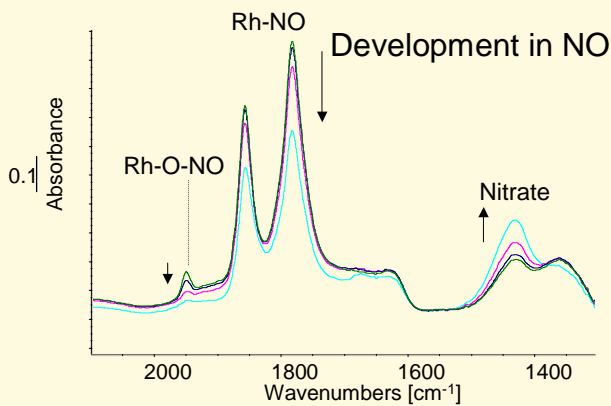
Noble metals

0.35 wt% Rh
2.3 wt% Co

- Rhodium is inhibited by traces of NO
- Addition of Cobalt improves activity



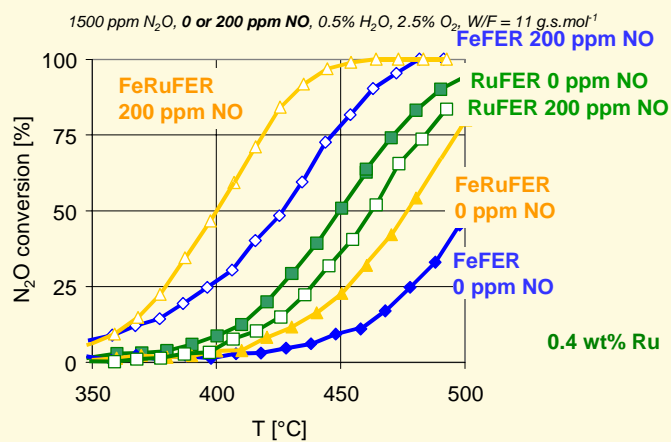
In situ FTIR – NO adsorption at 350 °C on Rh-ZSM-5



Noble metals

- NO adsorbs strongly Rh at 350°C
- Nitrates are formed

Combination of Fe en Ru



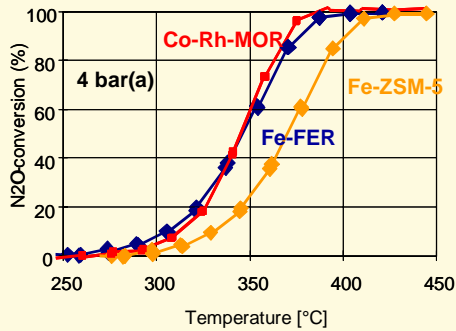
Noble metals

- Addition of Fe to Ru catalyst improves activity

Larger-scale tests of Co-Rh-MOR and Fe-FER and Fe-ZSM-5

TU Delft

500 ppm N₂O, 200 ppm NO, 0.5% H₂O, 2.5% O₂, S.V. = 8500 hr⁻¹



➤ Co-Rh-MOR and Fe-FER have about equal activity under realistic conditions

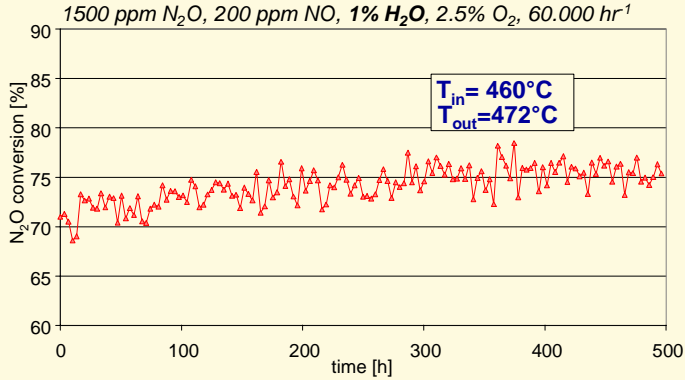
Noble metals

Iron Zeolites



Stability test under 'severe' conditions

TU Delft



➤ Co-Rh-MOR is stable for over 500 h

Noble metals



Conclusions iron zeolites



Iron Zeolites

- Relation between activity for N_2O decomposition and activity:
 - specific Fe^{2+} -species is involved in active site
 - concentration can be increased by preparation at $pH = 2.5$
- NO promotes N_2O decomposition
 - removal of adsorbed NO_2 left after N_2O decomposition



Conclusions noble metals



Noble metals

- NO inhibits N_2O decomposition
 - NO adsorption on active site, followed by formation of nitrates
- Combination of iron and ruthenium is promising

- Catalyst active at $350^\circ C$
- Stable for > 500 h
- Costs with Rh > 1.2 € per ton CO_2
 - costs much lower at higher temperatures
 - current price of CO_2 ca. 5 € per ton



Future plans



- Characterisation of promoted noble metals
 - *in situ* FTIR NO/N₂O reaction
 - Transient studies
- Lower amount of noble metal, improve Ru catalyst.
- Test in side-stream of a nitric acid plant

Noble metals

Iron Zeolites



Acknowledgements



- Novem, Ministry of the Environment of the Netherlands
- Javier Pérez-Ramírez (YARA)
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- Arjan Overweg, IRI Delft for Mössbauer measurements
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