

Direct decomposition of N₂O at low(er) temperature: the effect of NO, combining active metals and a synergistic effect

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Proceedings of the 19th North American Meeting of the North American Catalysis Society, Philadelphia, May 2005

Oral presentation

Direct decomposition of N₂O at low(er) temperature: the effect of NO, combining active metals and a synergistic effect

J.A.Z. Pieterse¹, G.D. Pirngruber², S.Booneveld¹, G. Mul³, I.M. Cabrera³ and R.W. van den Brink¹

¹ECN Clean Fossil Fuels, P.O Box 1, Westerduinweg 3, 1755 ZG, Petten, The Netherlands.

²ETH Swiss federal institute of technology, Rämistrasse 101 CH - 8092 Zurich, Switzerland

³Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands.

*pieterse@ecn.nl

Introduction

Direct catalytic decomposition of N₂O in the tail gases of nitric acid plants has been identified as a cost efficient and safe method for N₂O abatement. However, in many plants tail gas temperatures are not high enough to promote decomposition of N₂O. The current state-of-the-art catalysts for N₂O decomposition operate only when the tail-gas temperature is higher than 673 K [1]. The selective catalytic reduction (SCR) of N₂O with hydrocarbons is possible at temperatures of about 523 K and up, which is about the lowest possible tail gas temperature of a nitric acid plant. In the past various studies have been performed on the SCR of N₂O using NH₃, C₃ and C₄ or methane as a reducing agent. Combined NO_x and N₂O removal by means of HC-SCR has also been investigated. While SCR is feasible, the cost of the reducing agent makes it more expensive than other techniques [1]. Development of improved catalysts that convert N₂O at temperatures below 673 K without reducing agent is therefore attractive. Even if the temperature of the specific tail-gas is higher than this value, the improved catalysts would allow for smaller reactors, which is obviously also economically desirable. Iron-zeolites, especially Fe-ZSM-5, have been studied extensively for use as catalysts for N₂O decomposition [1]. NO_x, that is usually present in the off-gas, promotes N₂O decomposition over iron-zeolites. Fe-FER and Fe-BEA perform particularly well. However, a temperature of 673 K and elevated pressure are still necessary with Fe-FER in the presence of H₂O and NO_x to achieve 75 % N₂O conversion [1]. Noble metal catalysts have a higher intrinsic activity for N₂O decomposition in comparison to iron. Unfortunately, N₂O decomposition reaction over noble metal catalysts is inhibited by NO, O₂ and H₂O. This prevents their use in the tail gas of nitric acid factories. The present study shows, how on zeolites a synergistic effect between iron and ruthenium, can improve N₂O decomposition tremendously if some NO is present. This effect also manifests itself in the presence of O₂ and H₂O. This synergy provides new opportunities for the use of noble metal to catalyze N₂O decomposition in exhaust gases of nitric acid plants at temperatures lower than currently reported.

Materials and Methods

The sodium or ammonium form of zeolite FER, ZSM-5, MOR and BEA were obtained from Tosoh Inc., Sud-chemie and Zeolysts respectively. Wet-ion exchange was applied to exchange Na⁺ for NH₄⁺ and Ru(NH₃)₆³⁺ (0.4 wt% Ru). Iron was loaded with dry impregnation of iron nitrate (2 wt% Fe). The catalysts were calcined at 803 K for 3 hours using 3K/min. Activity measurements were carried out in a conventional micro-flow reactor (at atmospheric pressure) equipped with FTIR, a NO_x analyzer and GC. ICP/AES was used to determine metal content.

Results and Discussion

Figure 1 shows the effect of NO on RuFER, FeFER and FeRuFER. In the absence of NO, RuFER shows much higher conversion than FeFER. High activity of Ru-zeolite in the decomposition of N₂O was reported before. In the presence of 200 ppm NO FeRuFER shows by far the highest conversion.

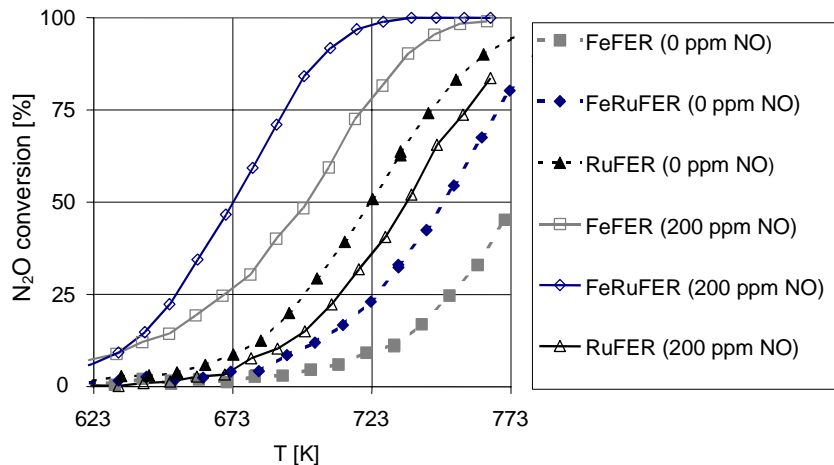


Figure 1 N₂O decomposition as function of the temperature over FeRuFER, RuFER, FeFER: 1500 ppm N₂O, 0 or 200 ppm NO, 0.5% H₂O, 2.5% O₂, W/F (STP) 11 g.s.mol⁻¹

Combining iron and ruthenium in FeRuFER results in a conversion much higher than the sum of the individual monometallic analogues, i.e. a synergy between the metals is responsible. Figure 2 shows NO_x profiles. FeFER produces NO₂ beyond equilibrium by reaction of N₂O and NO. Strikingly, FeRuFER does show similarities with RuFER but not with FeFER [2].

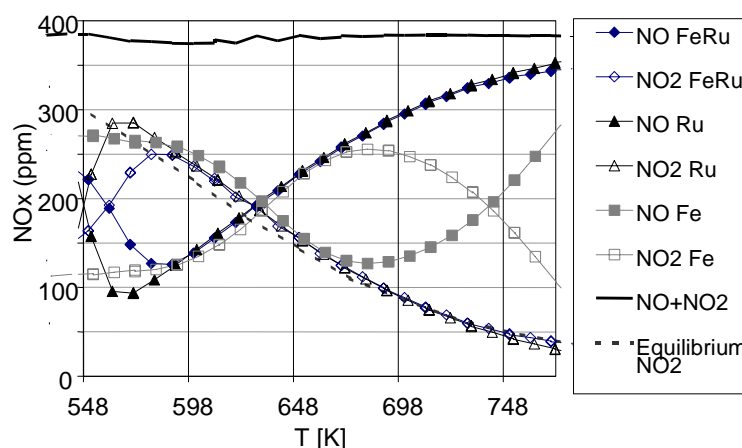


Figure 2. FeRuFER, RuFER, FeFER. NO-NO₂ concentration versus temperature: 1500 ppm N₂O, 400 ppm NO, 2 % O₂, W/F (STP) 11 g.s.mol⁻¹. Equilibrium NO₂: NO + O₂ ⇒ NO₂

Ongoing research indicates similar behaviour with other zeolites and metals [2].

Significance

The synergy between metals in bimetallic catalysts for N₂O decompositions results in higher activity and improved cost efficiency of the reduction technology. The definition of structure-activity relations for these catalysts in N₂O decomposition in the presence of NO, O₂ and H₂O poses an interesting and challenging task.

References

1. Perez-Ramirez, J. Kapteijn, F. Schoffel K. and Moulijn, J.A. *Appl. Catal. B: Environ.* 44 117 (2003).
2. Pieterse, J.A.Z., Booneveld, S., Mul, G., Melian-Cabrera, I., Brink, van den R.W. *Cat. Letters*, 2004, in press



Energy research Centre of the Netherlands

Direct decomposition of N_2O at low(er) temperature: the effect of NO, combining active metals and a synergistic effect



Collaborations

J.A.Z Pieterse
R.W van den Brink
S. Booneveld



Gerhard D. Pirngruber



G. Mul
I.M. Cabrera



www.ecn.nl

Outline

- **N₂O emissions**
- **NO-assisted decomposition of N₂O for use in the tail gas of the nitric acid industry**
 - I. **Fe-ZSM-5: new insights**
 - II. **Fe-Ru-zeolite: a synergistic effect**

Nitrous oxide is a potent greenhouse gas

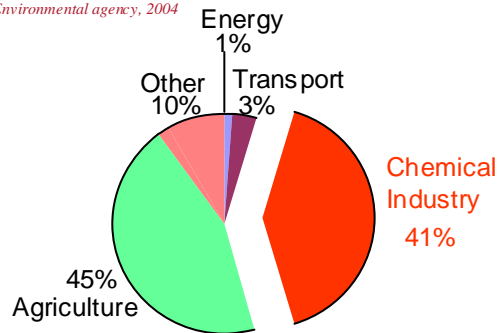
'N₂O is 310 times as effective in trapping heat in the atmosphere than CO₂ over a 100-year time period'



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

Nitric acid industry is an important source of N₂O

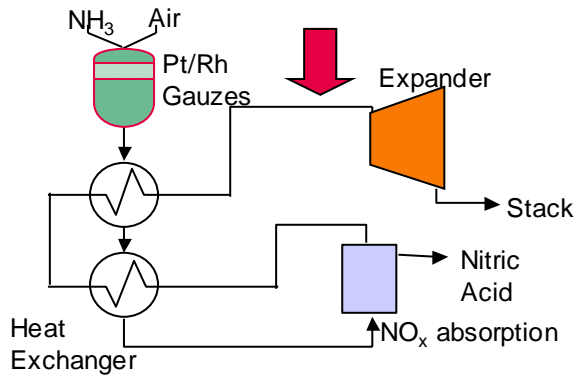
Source: European Environmental Agency, 2004



The Netherlands

Total N₂O Emission 15.3 Mton CO₂ eq.
or 7% of total GHG emissions

End-of-pipe removal of N₂O in nitric acid plant



Tail Gas :

500 – 3000 ppm N₂O
20 - 3000 ppm NO_x
1.5 – 3 % O₂
0.5 – 2% H₂O
P = 1 – 9 bar
T = 200 - 500°C

- ✓ Possible in all plants, cost efficient (0.5 – 3 € per ton CO₂), no effect on core process, combination with NO_x-removal possible

Goals at ECN

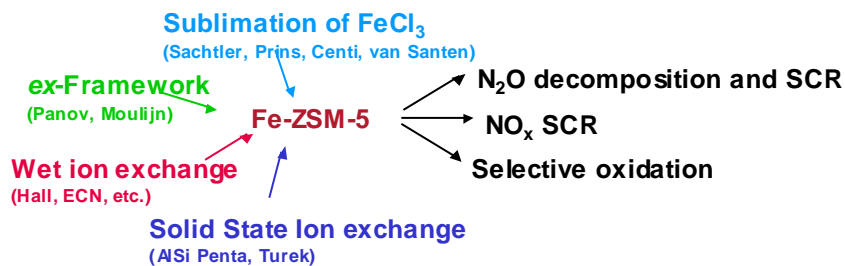


✓ Optimise catalysts for durable N_2O removal below 500°C in the tail gas of nitric acid plants

➤ Catalysts

- I. Fe - zeolite
- II. Noble metal zeolite
- III. Fe (Co) – noble metal zeolite

Different ways to prepare Fe-zeolite catalysts

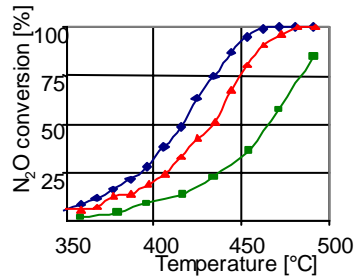


- Literature : a diversity of iron species in **All** samples, ' very little iron is active'
- Sublimation and ex-framework method most widely studied

➤ *Are 'complex' sublimation and synthesis methods better for N_2O decomposition than 'easy' ion-exchange ?*

Fe-ZSM-5 collected from ETH Zurich, Univ. Delft, Eindhoven

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



ECN Wet Ion Exch. (WIE)

Steam-CVD (TUe)*

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

	Si/Al	Fe wt%	Fe/Al
ECN Wet Ion Exch. (WIE)	11.5	2.3	0.37 [#]
Steam-CVD (TUe)*	19.4	3.6	0.97
ex-[Fe,Al]-ZSM-5**	31.5	0.7	0.15

[#] 50% is inactive Fe₂O₃

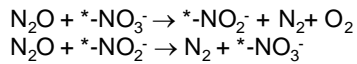
* Zhu, Hersen, Mojet, van Wolput, van Santen, Chem. Commun. (2002) 123

** Pérez-Ramírez, Mul, Kapteijn, Moulijn, Chem. Commun (2001) 693.
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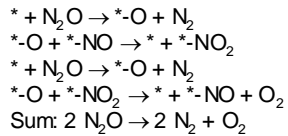
- WIE yields *superior* conversion *with tail gas* conditions: *Why?*
- *what is the relation between preparation and activity?*
 - Use of similar parent zeolites is necessary
 - Tail gas contains NO: Define the role of **NO-assisted** N₂O decomposition

- **NO increases N₂O decomposition activity via a catalytic effect**
- **two mechanism proposed in literature**

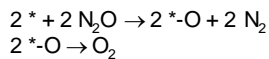
1. Sang & Lund 2001 (2004): via nitrate / nitrite



2. Mul et al. 2002: via adsorbed NO / NO₂



✓ **Conventional decomposition**



New study to find out:

- whether the beneficial effect of NO strongly varies with preparation method to explain the observed differences in activities among the samples
- more on the mechanism of NO-assisted N₂O decomposition

By:

- Using two very different parent ZSM-5 zeolites
- Both loaded with Fe via CVD and via WIE
- Study NO-assisted N₂O decomposition with *in-situ* FTIR/MS, pulse/step and steady state kinetic experiments

CVD and WIE Fe-ZSM-5 in NO-assisted N₂O decomposition

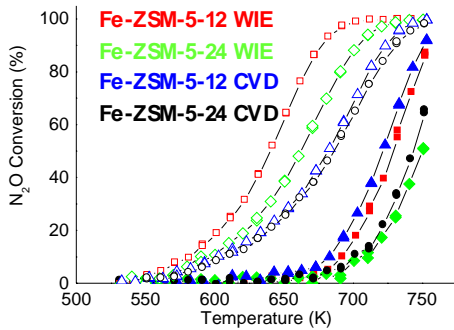
sample	Si/Al	Fe (wt%)	Fe/Al	Origin
Fe-ZSM-5-24 WIE	24	1	0.26	Süd chemie, template
Fe-ZSM-5-24 CVD	24	4.4	1.1	
Fe-ZSM-5-12 WIE	12	2.8	0.45	Alsi Penta, no template
Fe-ZSM-5-12 CVD	12	5.4	0.87	

CVD: O₂ at 773 K, FeCl₃ was sublimed at 593 K, washing, calcination at 773 K (J. Catal. 227 (2004) 164)
 WIE: FeSO₄·7H₂O at 353 K for 6 h in N₂, calcination at 773 K

two very different parent ZSM-5 zeolites

CVD and WIE Fe-ZSM-5 in NO-assisted N₂O decomposition

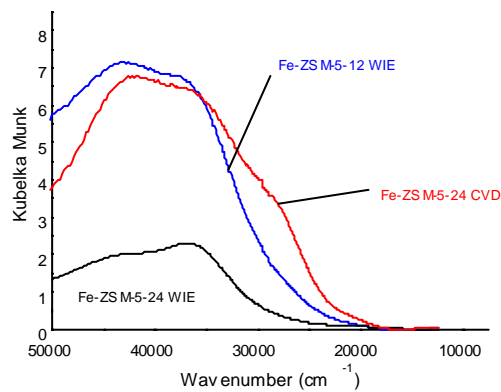
3000 ppm N₂O, 0 ppm NO (full symbol) 800 ppm NO (open symbols) balance N₂, GHSV = 60000 h⁻¹.



T 20% conv	with NO	without NO	diff
Fe-ZS M-5-12 WIE	331	432	-101
Fe-ZS M-5-24 WIE	350	451	-101
Fe-ZS M-5-12 CVD	360	422	-62
Fe-ZS M-5-24 CVD	367	447	-80

- catalytic effect of NO is larger for WIE than for CVD
- Structure-activity relation ?

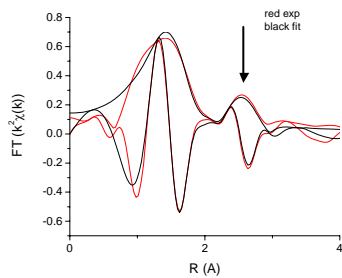
UV-Vis of CVD and WIE Fe-ZSM-5



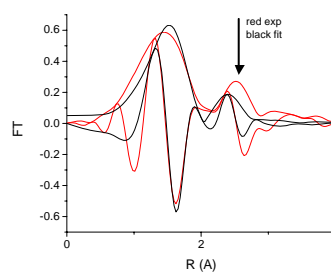
UV-Vis

- WIE: isolated iron ions CT 43000 cm⁻¹, 38000 cm⁻¹; (Lehmann, 1970)
- CVD: small clusters CT 27000 cm⁻¹

EXAFS characterisation Fe-ZSM-5-12 WIE



backscattering by Fe and O: good fit



backscattering by Al and O: poor fit

➤ Iron neighbor indicates dimers or oligonuclear clusters

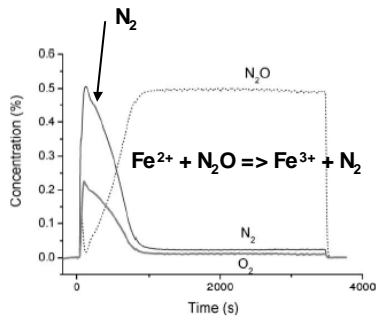
➤ UV/VIS: no oligonuclear clusters

➤ Dimers in WIE (clusters in CVD)

➤ Catalytic effect of NO is larger for *dimers and isolated ions (WIE)* than for *clusters (CVD)*

➤ Pirngruber, J. Catal. 224 (2004) 429:

➤ **Isolated ions and dimers reduce more easily to Fe²⁺**



Step-response experiment:

➤ WIE: N₂/Fe 0.05

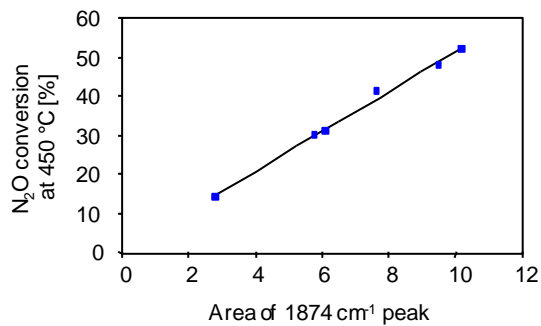
➤ CVD: N₂/Fe 0.02

➤ **WIE has higher amount of Fe²⁺**

Fig. 7. Step response of Fe-ZSM-5 CVD at 673 K, 5000 ppm N₂O, GHSV = 20,000 h⁻¹.

➤ Mul et al. 2003: **FTIR of adsorbed NO**

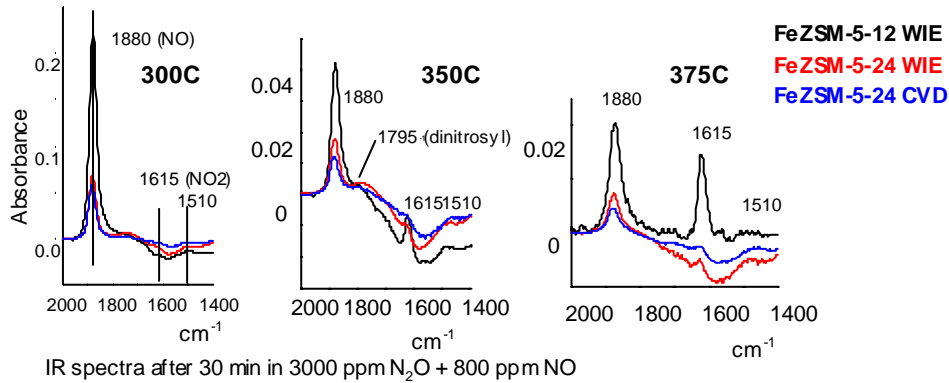
1874 cm⁻¹ = Fe²⁺-NO



➤ **correlation between activity and Fe²⁺-NO**

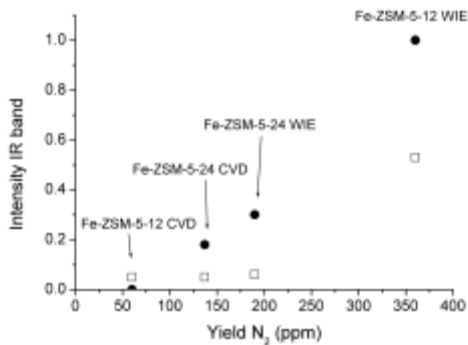
➤ **Do our WIE samples have more Fe²⁺ sites than our CVD samples?**

FTIR/MS study NO-assisted N₂O decomposition with Fe-ZSM-5



- 1880 cm⁻¹ nitrosyl, 1615 cm⁻¹ weakly bound NO₂ (desorbs in He)
- NO and NO₂ surface coverage indeed higher for WIE than for CVD

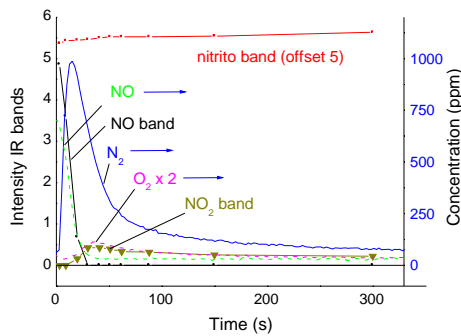
• 1880,1615 cm⁻¹ vs. activity



Yield of N₂ achieved in the in situ IR experiments at 648 K vs. the intensity of the bands of NO (circles) and NO₂ (squares), GHSV = 120000 h⁻¹.

- the catalytic activity correlates well with the concentration of adsorbed NO
 - synthesis history of parent zeolites is not important: activity normalized on Fe is similar
- WIE gives a higher activity for NO-assisted N₂O decomposition than CVD because they contain a higher fraction of Fe²⁺ sites

The mechanism of NO-assisted N₂O decomposition



Pulse and step experiments

Step from 800 ppm NO to 3000 ppm N₂O in He at 350C in the IR reactor. Fe-ZSM-5-12 WIE, GHSV ~120000 h⁻¹.

- NO₂ band correlates with the O₂ formation
- NO and NO₂ are part of catalytic cycle
- Nitrito bands intensity behaves as spectator species
- Nitrito are apparently not part of the catalytic cycle

Remarks Fe-ZSM-5

The catalytic effect of NO is significantly larger for our Fe-ZSM-5 samples prepared by wet ion exchange than for those prepared by chemical vapor deposition

Our ion-exchanged Fe-ZSM-5 samples have a higher activity for NO assisted N₂O decomposition because they contain a higher fraction of Fe²⁺ sites (from dimer and isolated sites)

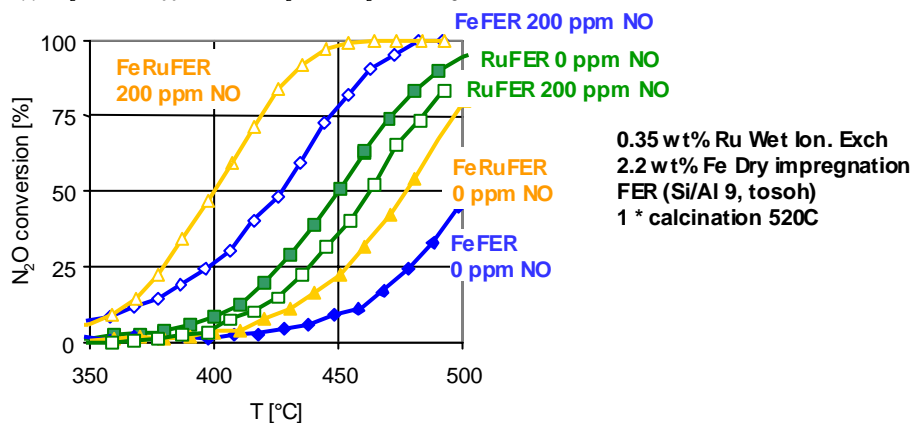
Adsorbed NO and NO₂ are part of the mechanism of NO-assisted N₂O decomposition with our Fe-ZSM-5

Iron-Ruthenium-FER

FeRuFER

NO-assisted N₂O decomposition over Fe-Ru-FER

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



- In the presence of NO, conversion FeRu >> Fe + Ru
- **A synergistic effect increases the activity**

How to explain synergy Fe and Ru in FeRuFER

- Possibility:

The adsorption properties for NO change:

is Iron trapping NO to free Ru sites for N₂O decomposition?

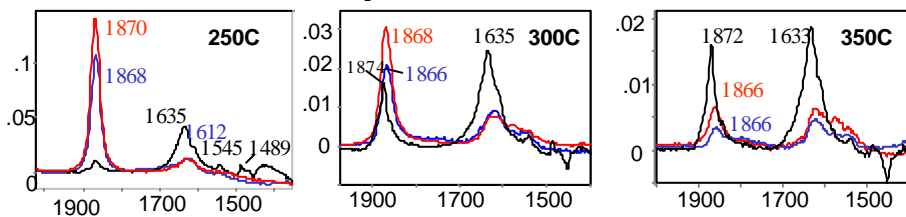
Fe-FER: Activity higher in the presence of NO

Ru-FER: Activity lower in the presence of NO

Adsorption properties of NO

➤ FTIR study NO-assisted N₂O decomposition with **FeFER**, RuFER and **FeRuFER**

IR spectra after 30 min in 3000 ppm N₂O + 800 ppm NO



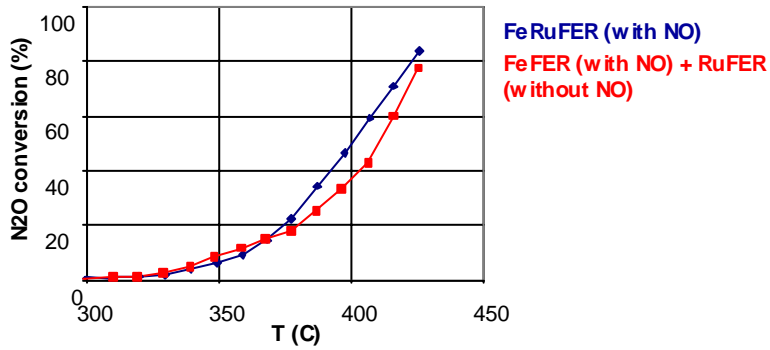
Stable nitrates are formed on RuFER, not on FeRuFER

IR spectra of FeRuFER closer to FeFER than to RuFER

➤ NO adsorbs on Fe, i.e. inhibition of NO on Ru is reduced by Fe

➤ **conversion FeRu with NO should approach the sum of (Fe with NO) + (Ru without NO)**

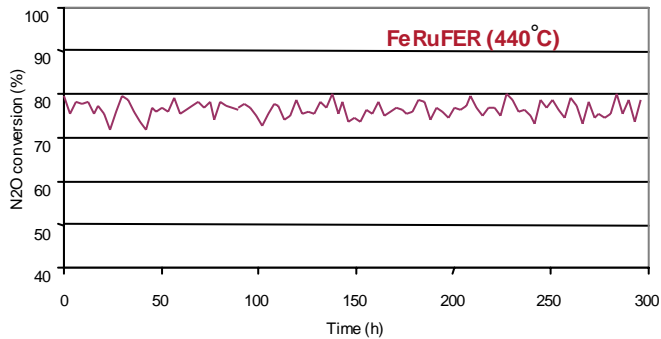
Sum of FeRuFER (with NO) and RuFER (without NO)



➤ reasonable close match

▪ Durability of FeRuFER

1500 ppm N₂O, 200 ppm NO, 1% H₂O, 2.5% O₂, 60.000 hr⁻¹



➤ FeRuFER, (FeRuBEA,..) are active and stable catalysts

Conclusions/Remarks FeRuFER

A synergistic effect in FeRuFER was found to increase the activity for NO assisted N₂O decomposition tremendously

The synergy seems best explained by a change in the adsorption properties of NO (**research continues**)

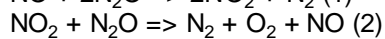
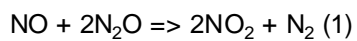
Iron-ruthenium-zeolites are good, cost-efficient catalysts for N₂O decomposition *in the presence of NO*

How to explain synergy Fe and Ru in FeRuFER

- 1) The adsorption properties for NO change: Iron is trapping NO
Fe-FER: Activity higher in the presence of NO
Ru-FER: Activity lower in the presence of NO

- 2) Two parallel (catalytic) reactions:

Iron:



Second (parallel) reaction path to close the cycle (create O₂) and start the cycle on Fe (form NO)