

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

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

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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 [1, 2, 3]. Fe-FER [2] and Fe-BEA [4] perform particularly well for N₂O decomposition. However, a temperature of 673 K is still necessary with Fe-FER in the presence of H₂O and NO_x to achieve 75 % N₂O conversion [2]. In the present study, we show how combining iron with ruthenium can increase N₂O decomposition activity in exhaust gas that contains NO.

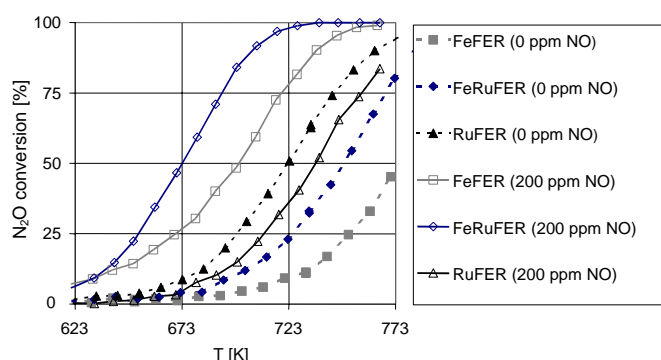


FIG 1: N₂O decomposition as function of the temperature over FeRuFER, RuFER FeFER: 1500 ppm N₂O, 0 or 200 ppm NO, 0.5% H₂O, 2.5% O₂, W/F (STP) 11 g.s.mol⁻¹

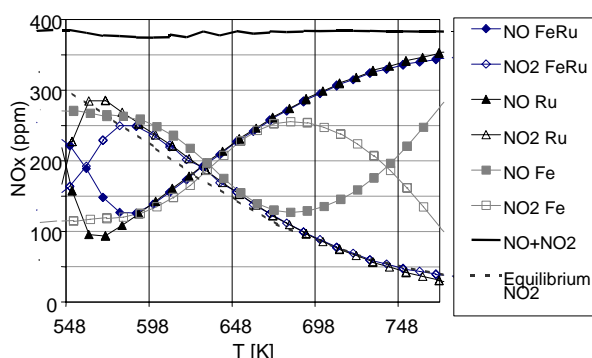


FIG 2: FeRuFER, RuFER, FeFER. NO-NO₂ concentration versus temperature: 1500 ppm N₂O, 400 ppm NO, 2 % O₂, W/F (STP) 11 g.s.mol⁻¹. Equilibrium NO₂: NO + O₂ => NO₂

Figure 1 shows the effect of NO on RuFER, FeFER and FeRuFER. In the absence of NO, RuFER shows much higher conversion than FeFER. In the presence of 200 ppm NO FeRuFER shows by far the highest conversion. 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 by reaction of N₂O and NO [5]. Strikingly, FeRuFER does show similarities with RuFER but not with FeFER [6]. Ongoing research shows similar behaviour with other zeolites and metals.

[1] R. Maurer, M. Groves in: Reduction of N₂O emissions from HNO₃ plants, results from a pilot plant, Proceeding of the NO_xConf2001, 2001, Paris, France.

[2] B. Neveu, C. Hamon and K. Malefant, French Patent WO 99/34901.

[3] J. Perez-Ramirez, F. Kapteijn, K. Schoffel and J.A. Moulijn, Appl. Catal. B:Environ. 44 (2003) 117.

[4] J.A.Z. Pieterse, S. Booneveld and R.W. van den Brink, App. Catal. B:Environ. 51 (2004) 215.

[5] J. Perez-Ramirez, G. Mul, F. Kapteijn and J.A.Moulijn, J. Catal. 208 (2002) 211.

[6] J.A.Z. Pieterse, S. Booneveld, G.Mul, I. Melian-Cabrera, R.W. van den Brink, Catal. Lett. 99 1 (2005) 41.

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Outline

- N_2O emissions
- NO-assisted decomposition of N_2O 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

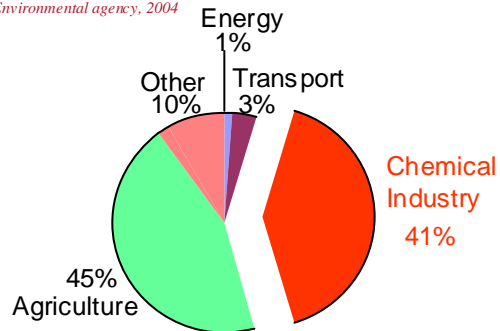
'N₂O is 310 times as effective in trapping heat in the atmosphere than CO₂ over a 100-year time period'



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

Nitric acid industry is an important source of N₂O

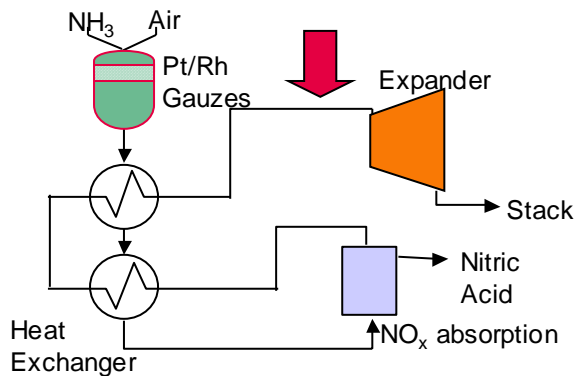
Source: European Environmental agency, 2004



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

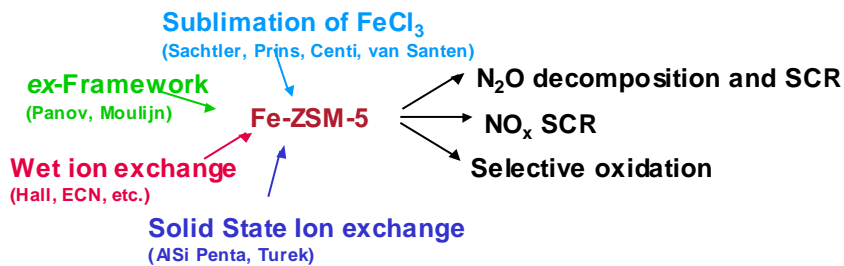


- ✓ Optimise catalysts for durable N₂O removal below 500 °C in the tail gas of nitric acid plants

➤ Catalysts

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

Different ways to prepare Fe-zeolite catalysts

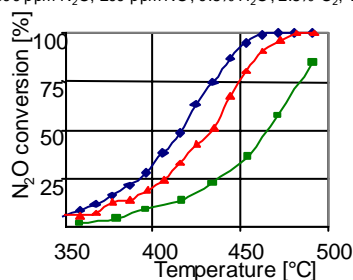


- Literature : a diversity of iron species in **All** samples, ' very little iron is active'
- Sublimation and ex-framework method most widely studied

➤ 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 N_2O , 200 ppm NO , 0.5% H_2O , 2.5% O_2 , $WF = 11 \text{ g.s.mol}^{-1}$



ECN Wet Ion Exch. (WIE)

Steam-CVD (TU/e)*

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

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

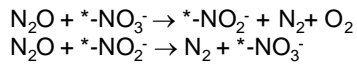
[#] 50% is inactive Fe_2O_3

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

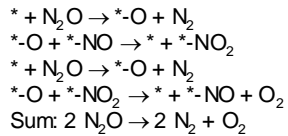
- WIE yields superior conversion with tail gas conditions: Why?
- what is the relation between preparation and activity ?
 - Use of similar parent zeolites is necessary
 - Tail gas contains NO : Define the role of **NO-assisted** N_2O decomposition

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

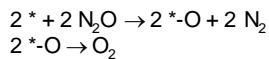
1. Sang & Lund 2001 (2004): via nitrate / nitrite



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

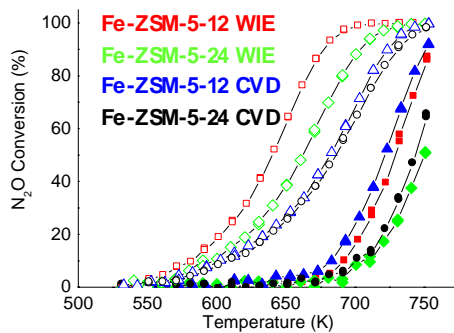
sample	Si/Al	Fe (wt%)	Fe/Al	Origin
Fe-ZSM-5-24 WIE	24	1	0.26	Süd chemie, template
Fe-ZSM-5-24 CVD	24	4.4	1.1	
Fe-ZSM-5-12 WIE	12	2.8	0.45	Alsi Penta, no template
Fe-ZSM-5-12 CVD	12	5.4	0.87	

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

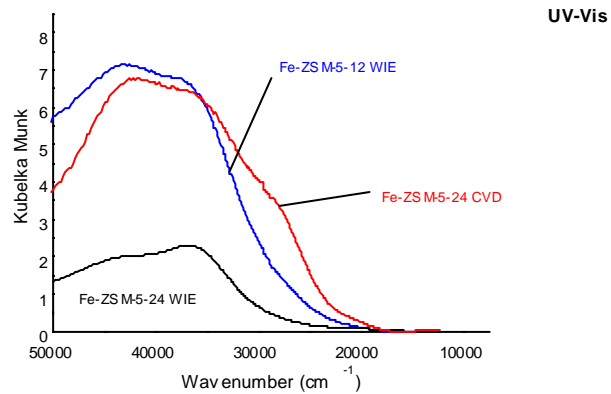
3000 ppm N₂O, 0 ppm NO (full symbol) 800 ppm NO (open symbols) balance N₂, GHSV = 60000 h⁻¹.



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

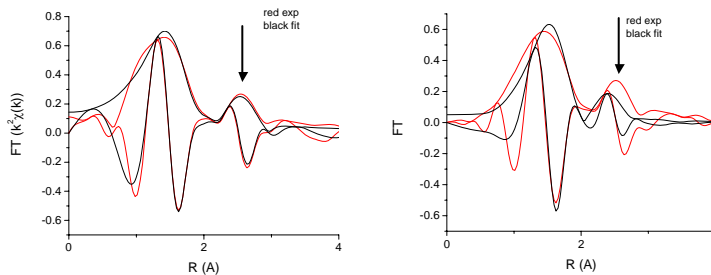
- catalytic effect of NO is larger for WIE than for CVD
- Structure-activity relation ?

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



- 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

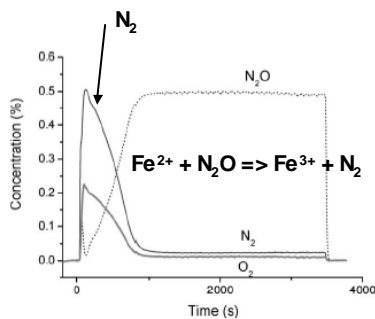
backscattering by Al and O: poor fit

- 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:

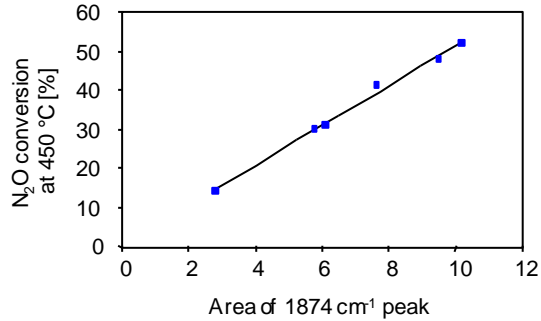
- WIE: N₂/Fe 0.05
- CVD: N₂/Fe 0.02

- **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**

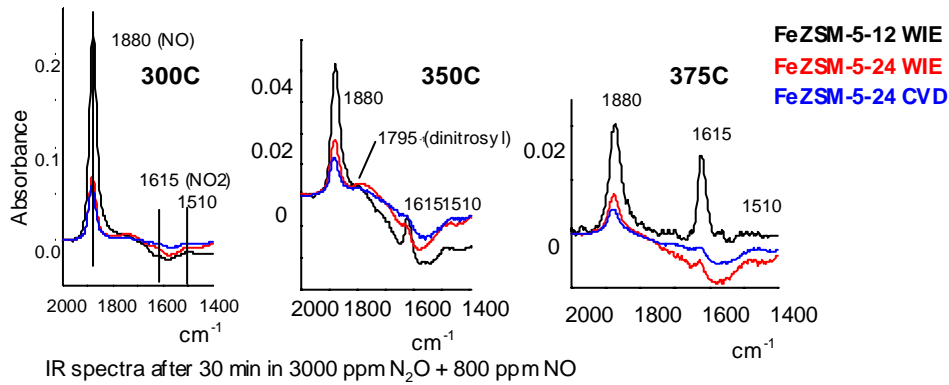
1874 cm⁻¹ = Fe²⁺-NO



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

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

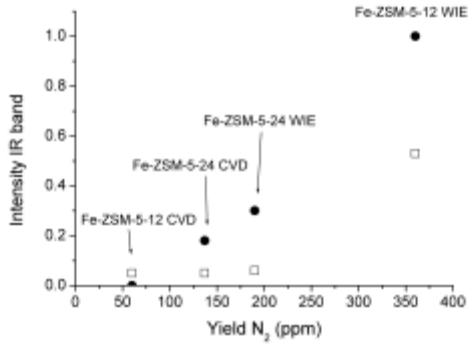
FTIR/MS study NO-assisted N₂O decomposition with Fe-ZSM-5



▪ **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**

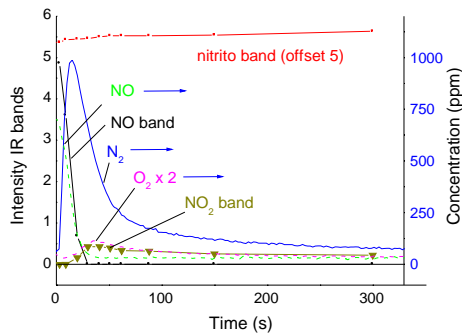
• 1880,1615 cm^{-1} vs. activity



Yield of N_2 achieved in the in situ IR experiments at 648 K vs. the intensity of the bands of NO (circles) and NO_2 (squares), GHSV $\sim 120000 \text{ h}^{-1}$.

- 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 N_2O decomposition than CVD because they contain a higher fraction of Fe^{2+} sites

The mechanism of NO-assisted N_2O decomposition



Pulse and step experiments

Step from 800 ppm NO to 3000 ppm N_2O in He at 350C in the IR reactor. Fe-ZSM-5-12 WIE, GHSV $\sim 120000 \text{ h}^{-1}$.

- NO_2 band correlates with the O_2 formation
- NO and NO_2 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)

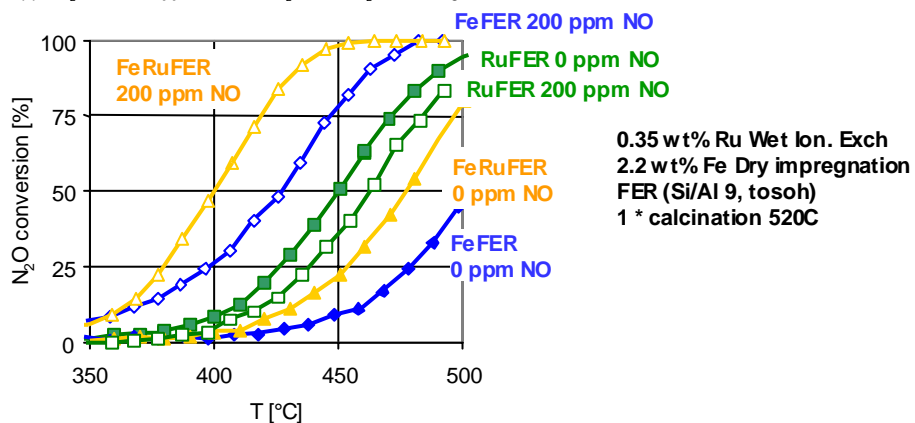
Adsorbed NO and NO₂ are part of the mechanism of NO-assisted N₂O decomposition with our Fe-ZSM-5

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?

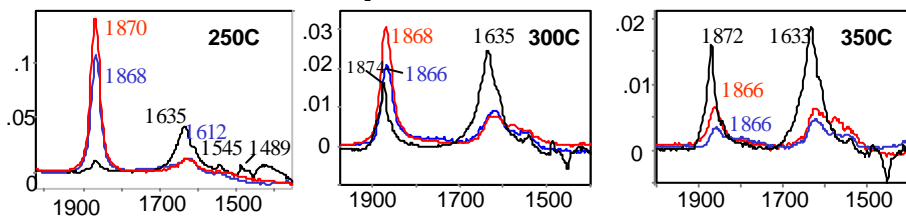
Fe-FER: Activity higher in the presence of NO

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



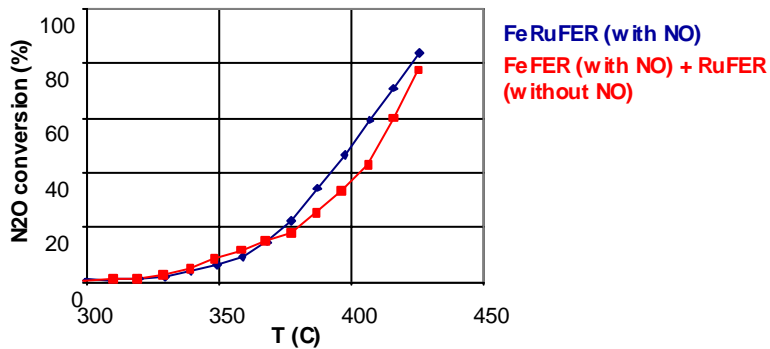
Stable nitrates are formed on RuFER, not on FeRuFER

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)**

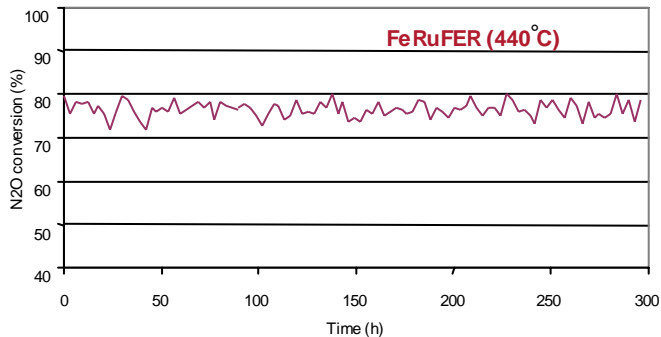
Sum of FeRuFER (with NO) and RuFER (without NO)



➤ 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**)

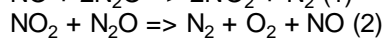
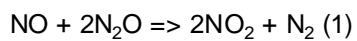
Iron-ruthenium-zeolites are good, cost-efficient catalysts for N₂O decomposition *in the presence of NO*

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)

Acknowledgements

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