Making and treating NO_x formed in NH_3 engines

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- NH_3 as a fuel *and* deNO_x agent
- N_2O advantages and disadvantages
- Acronyms SNCR, SCR, SCO
- SCR and its targets (3 reactions)
- Three surfaces (including LNT): M-Zeolites, MO, MO/M_{noble}
- SNCR example
- SCO, ammonia-slip abatement

NH_3 a fuel and deNO$_x$, both at once

NH_3 as a fuel
- accessible (Haber-Bosch, wind to NH_3, etc.)
- storable (*l*, g, and s)
- favorable ΔH, ΔG

$$2NH_3(g) + {}^3/_2O_2(g) \rightarrow \boxed{N_2(g)} + 3H_2O(g)$$

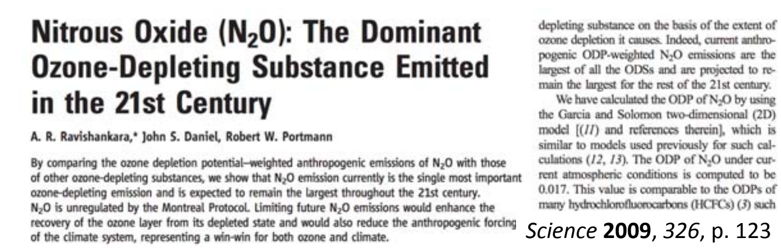
NH_3 in deNO$_x$
- storable
- oxidizable, NO_x reducing

NH_3 sources: biproduct, urea, primary fuel

Similar claims with HC's but storage differs from NH_3.

N_2O a double-edged environmental sword

Gas	20-y GWP*
CO_2	1
CH_4	72
N_2O	289
CFC-*freon*	11,000


Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

By comparing the ozone depletion potential–weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

depleting substance on the basis of the extent of ozone depletion it causes. Indeed, current anthropogenic ODP-weighted N_2O emissions are the largest of all the ODSs and are projected to remain the largest for the rest of the 21st century.

We have calculated the ODP of N_2O by using the Garcia and Solomon two-dimensional (2D) model [(*11*) and references therein], which is similar to models used previously for such calculations (*12*, *13*). The ODP of N_2O under current atmospheric conditions is computed to be 0.017. This value is comparable to the ODPs of many hydrochlorofluorocarbons (HCFCs) (*3*) such

Science **2009**, *326*, p. 123

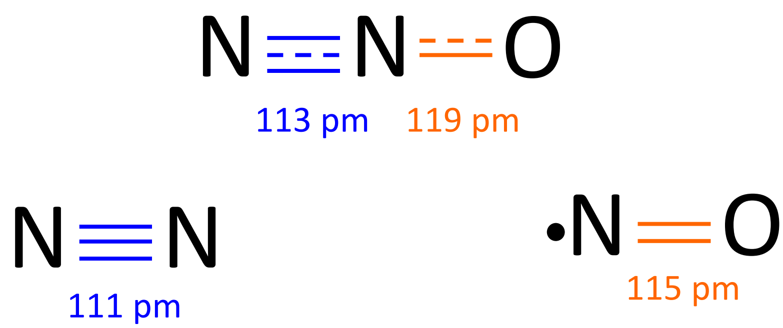
**IPCC Fourth Assessment Report: Climate Change* 2007, Sec. 2.10.2

Qualities unique to N_2O

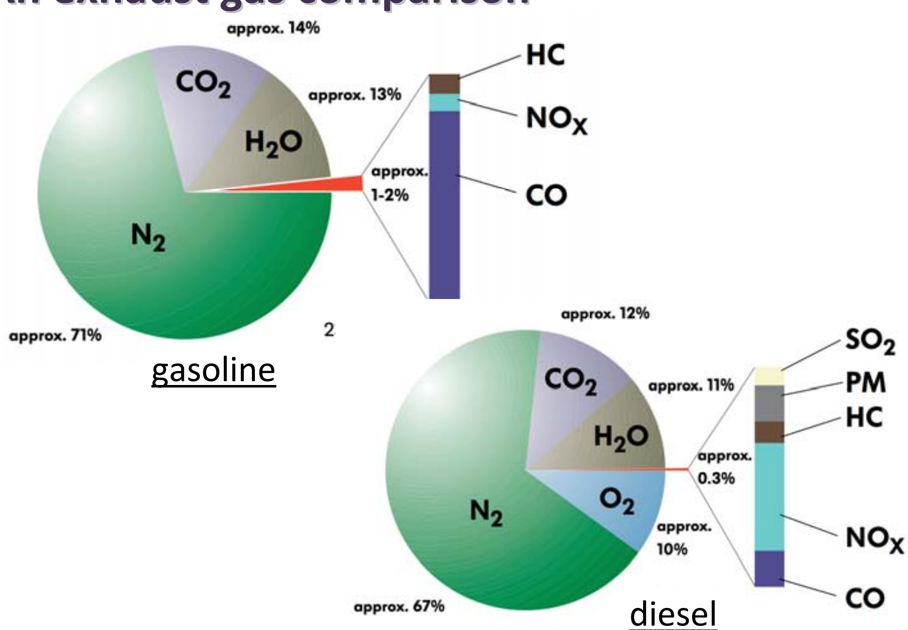
No other common NO_x has:

1. A strong N=N bond (high GWP)

2. Simple O transfer leading to N_2 (ozone depleter)

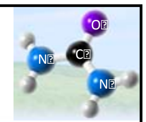


An exhaust gas comparison

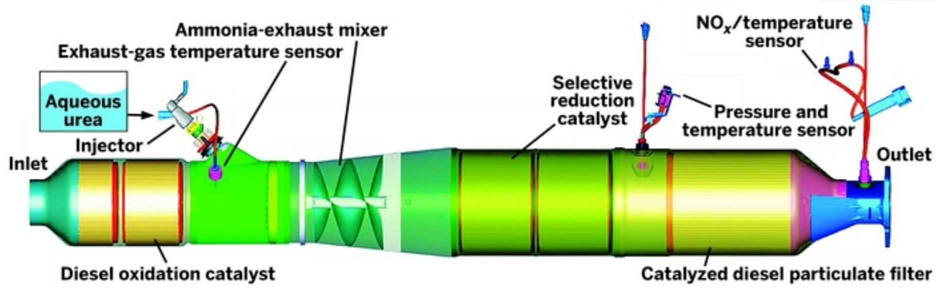


Volkswagon Motor Vehicle Exhaust Emissions Self-Study Programme Jan. 2000 www.volkspage.net/technik/ssp/ssp/SSP_230.pdf

Diesel Exhaust Fluid ("Hippy Juice")



Urea → NH_3 conversion limited at lower T



"Reducing NO_x in diesel engine exhaust presents a special chemistry challenge because of the oxidizing nature of the exhaust stream."

"…unlike sophisticated chemical plants…operated by…trained engineers, …catalytic converters can be turned on and turned off by anyone who can handle a car key."

Chem. & Eng. News, 5/21/2012 p 10

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Acronyms in ammonia exhaust chemistry

SCR: Selective catalytic reduction (of NO_x) by …

SNCR: Selective *noncatalytic* reduction (of NO_x) by …

$$2NH_3 + NO + O_2 \rightarrow 3H_2O + {}^3/_2N_2$$

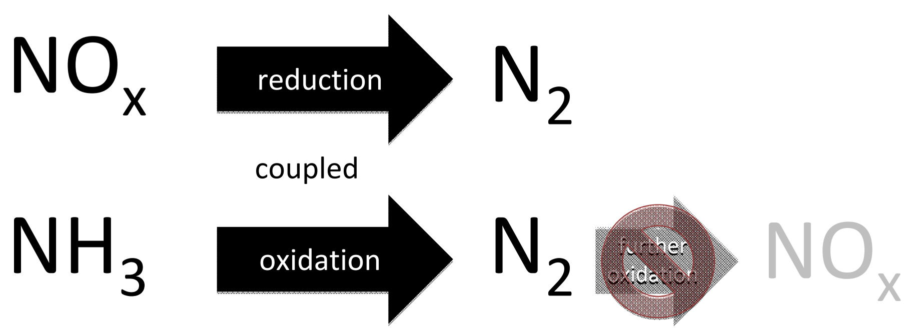
SCO: *Selective* catalytic oxidation (of NH_3)

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

LNT: Lean NO_x traps

$$MO + 2NO_x \rightarrow M(NO_n)_2(s) \text{ then SCR or SNCR}$$

Goals of SCR using NH_3



at lower T: formed NO reduced by NH_3 (SCR)

at higher T: some NH_3 lost to NO

higher E_A reached

less NH_3-cat absorption

Cu-zeolite

(NH_3) urea

Pant, A.; Schmieg, S. J. *Ind. Eng. Chem. Res.* **2011**, *50*, 5490–5498

Selective catalytic reduction (SCR) by NH_3

Standard

$$4NH_3\text{-cat} + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

Fast

$$2NH_3\text{-cat} + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$

Slow

$$4NH_3\text{-cat} + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$$

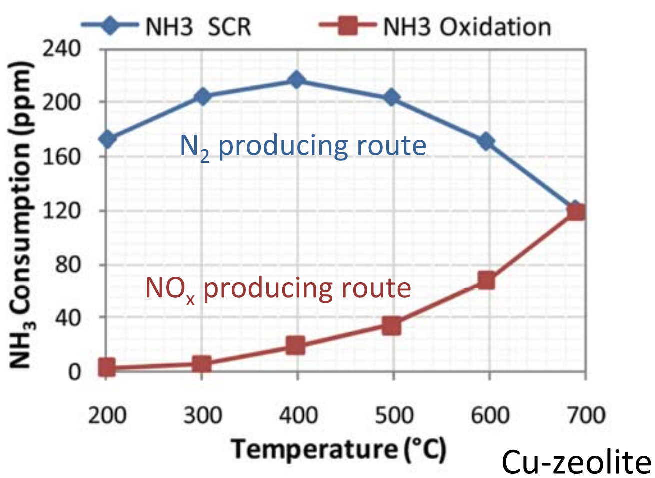
increasing [NO_2]

$$Rate_{fast} > Rate_{std} >> Rate_{slow}$$

~10x

Pant, A.; Schmieg, S. J. *Ind. Eng. Chem. Res.* **2011**, *50*, 5490–5498
M. Crocker *Development of Nitric Oxide Oxidation Catalysts for the Fast SCR Reaction* DOE June 2005.

Competition for NH_3: oxidation (to NO_x) vs SCR



Cu-zeolite

Figure 4. Relative NH_3 SCR and oxidation. Laboratory reactor data: inlet condition 200 ppm NOx, 5% NO_2 and NH_3 to NOx ratio of 1.2 at 30 kh^{-1} space velocity. Lines represent the trend.

Pant, A.; Schmieg, S. J. *Ind. Eng. Chem. Res.* **2011**, *50*, 5490–5498
Yuan, R. –M.; Fu, G.; Xu, X.; Wan, H. –L. *J. Phys. Chem. C* **2011**, *115*, 21218–21229

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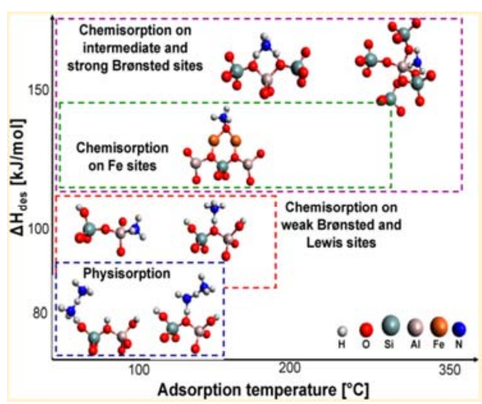
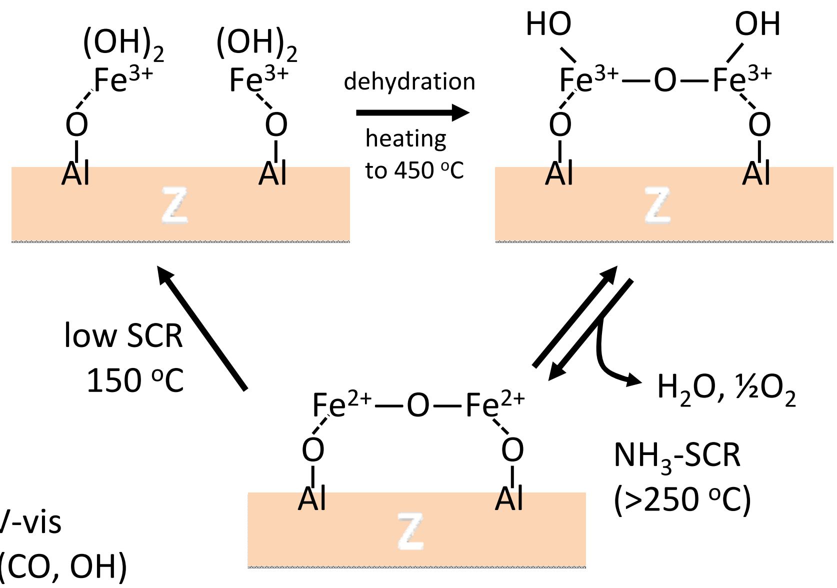
First row T.M. zeolite advantages

- T.M. ion (Fe^{3+}, Cu^{2+}) doped alumino-silicates
  Zeol = BEA, MOR, ZSM
- Imparts redox-active cycling
- Variable coordination
  - Brønsted (O-H···NH_x)
  - Lewis ($M \leftarrow :NH_x$)



Colombo, M.; Nova, I.; Tronconi, E *Catal. Today* **2010**, *151*, 223-230.
Skarlis, S. A.; Berthout, D.; Nicolle, A.; Dujardin, C.; Granger, P. *J. Phys. Chem. C* **2013**, *117*, 7154–7169.

Reduced, cooperative Fe(II) during NH_3 SCR



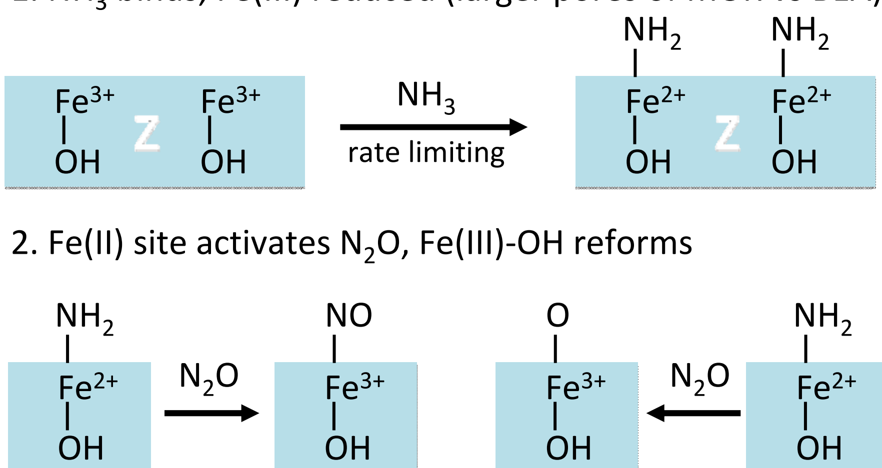
UV-vis
IR(CO, OH)
EXAFS

Kim, J.; Jentys, A.; Maier, S. M.; Lercher, J. A. *J. Phys. Chem. C* **2013**, *117*, 986–993.

SCR of N_2O by NH_3 over Fe-MORzeolites

1. NH_3 binds, Fe(III) reduced (larger pores of MOR vs BEA)

2. Fe(II) site activates N_2O, Fe(III)-OH reforms



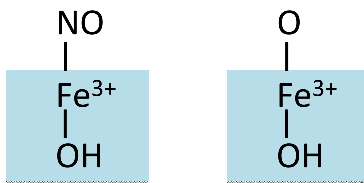
300 – 400 °C, IR, MS measurements

Zhang, X.; Shen, S.; He, C.; Ma, C.; Cheng, J.; Li, L.; Hao, Z. *ACS Catal.* **2012**, *2*, 512–520

SCR of N_2O by NH_3 over Fe-MORzeolites

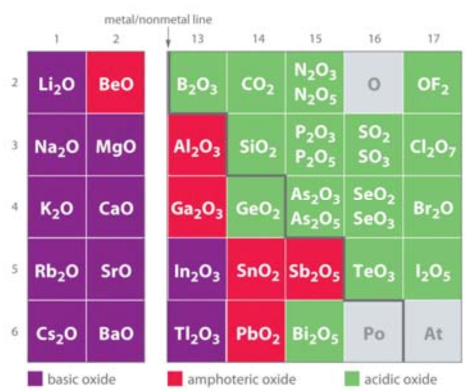
1. NH_3 binds, Fe(III) reduced
2. Fe(II) site activates N_2O, Fe(III)-OH reforms
3. (a) $H_2N + NO \rightarrow H_2NNO \rightarrow N_2 + H_2O$
   (b) $NO + O \rightarrow NO_2 \rightarrow N_2 + H_2O$ (by NH_3 SCR)

NH_3 altered mechanism: less N_2O decomposition, more reduction by



Zhang, X.; Shen, S.; He, C.; Ma, C.; Cheng, J.; Li, L.; Hao, Z. *ACS Catal.* **2012**, *2*, 512–520

Metal-oxides: acid/base properties



■ Desirable for LNT's

Some have accessible redox: TiO_2 V_2O_5 CeO_2

V_2O_5 MoO_3 WO_3

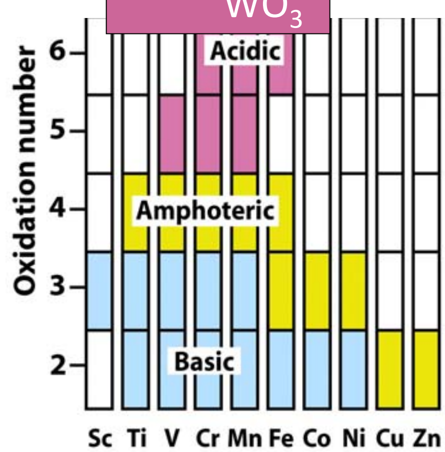


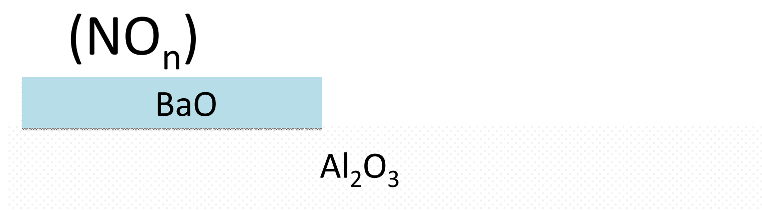
Figure 4-5
Shriver & Atkins Inorganic Chemistry, Fourth Edition

A lean NO_x trap (LNT) coupled with Pt

- trapped NO_x + NH_3
  $M(NO_n)_2$ selective toward N_2 (less N_2O)

$$BaO + 2NO + O_2 \rightarrow Ba(NO_2)_2$$

$$BaO + 2NO_2 + \tfrac{1}{2}O_2 \rightarrow Ba(NO_3)_2$$



*N-labeled studies

Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

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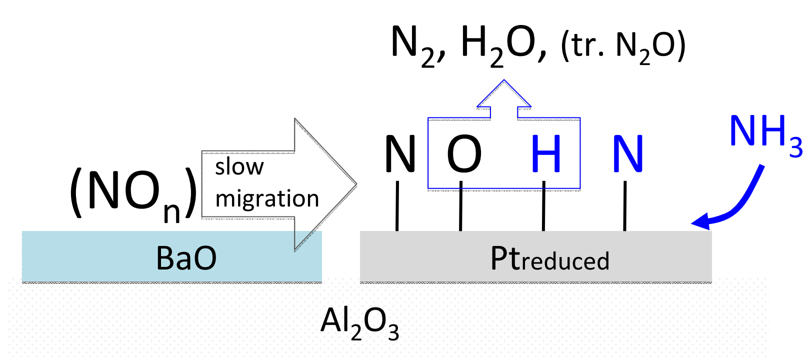


*N-labeled studies

Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

Evidence for N-N formation

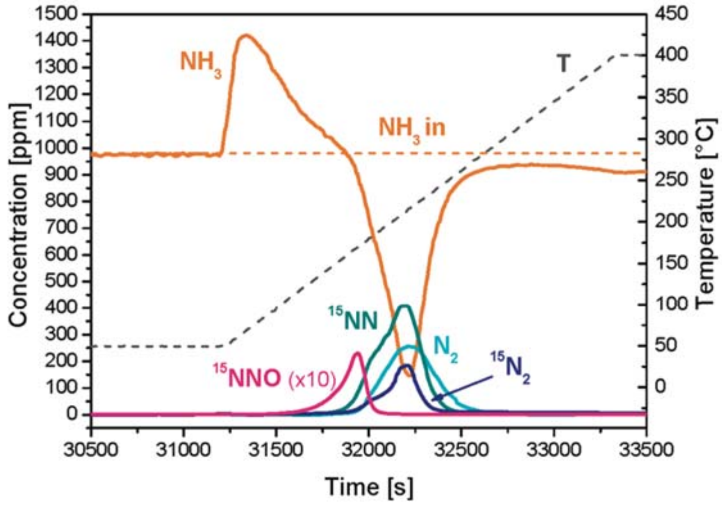
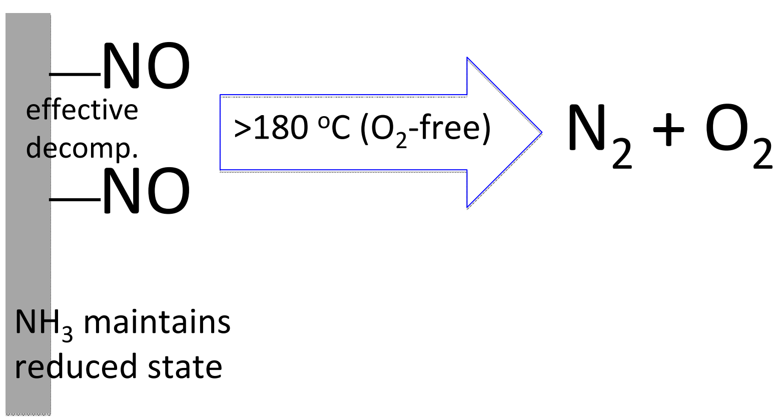


Figure 2. TPSR run with NH_3 (1000 ppm) after $^{15}NO_x$ adsorption at 150 °C (1000 ppm ^{15}NO + O_2 3% v/v in He) over Pt−Ba/Al_2O_3 catalyst.

Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

A lean NO_x trap (LNT) coupled with Pt

- trapped NO_x + NH_3
  - $M(NO_n)_2$ selective toward N_2 (less N_2O)
- higher T, reduced environment (less N_2O)



Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

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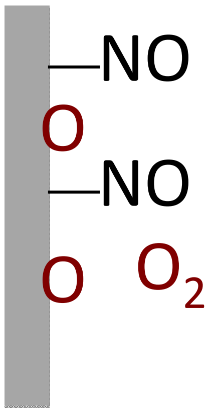
- trapped NO_x + NH_3
  $M(NO_n)_2$ selective toward N_2 (less N_2O)
- higher T, reduced environment (less N_2O)
- additional NO(g)/lower T or more O_2 (more N_2O)



leads to more N_2O

Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

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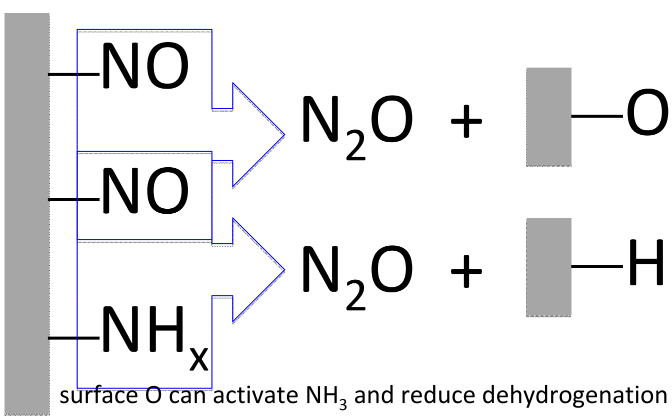


surface O can activate NH_3 and reduce dehydrogenation

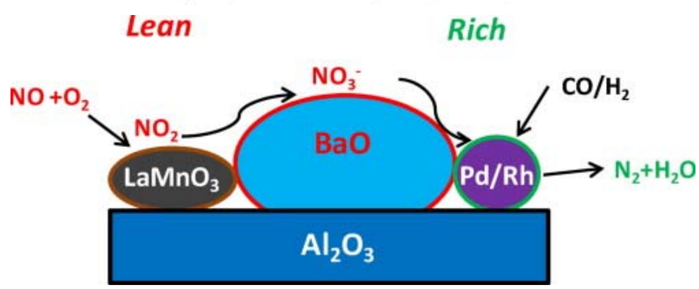
Lietti, L.; Artioli, N.; Righini, L.; Castoldi, L., Forzatti P. *Ind. Eng. Chem. Res.* **2012**, *51*, 7597–7605.

Another LNT catalyst ("Pt-free")

Catalysis Today
Volume 184, Issue 1, 30 April 2012, Pages 72–77
Catalytic Control of Lean-Burn Engine Exhaust Emissions

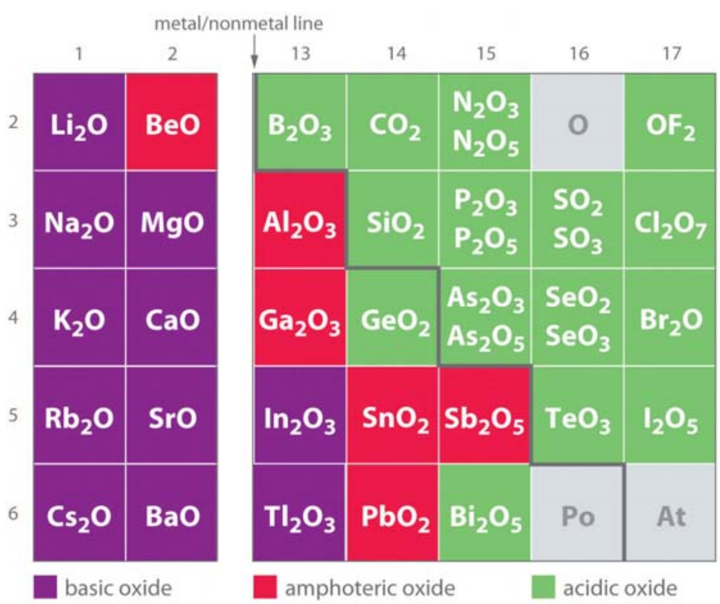
Pt-free, $LaMnO_3$ based lean NO_x trap catalysts

Gongshin Qi, Wei Li
General Motors Global Research & Development, 30500 Mound Road, Warren, MI 48090, United States



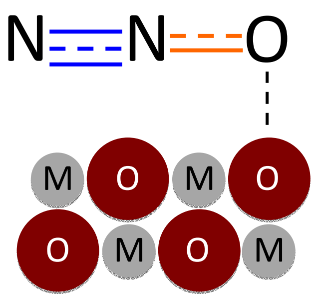
Qi, G.; Li, W. *Catalysis Today* **2012**, *184*, 72-77.

Exploiting metal-oxide basic properties

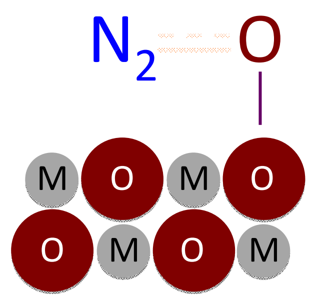


Mechanism of N_20 decomposition on MO

MO = Mg, Ca, Sr oxides



classic basic MO



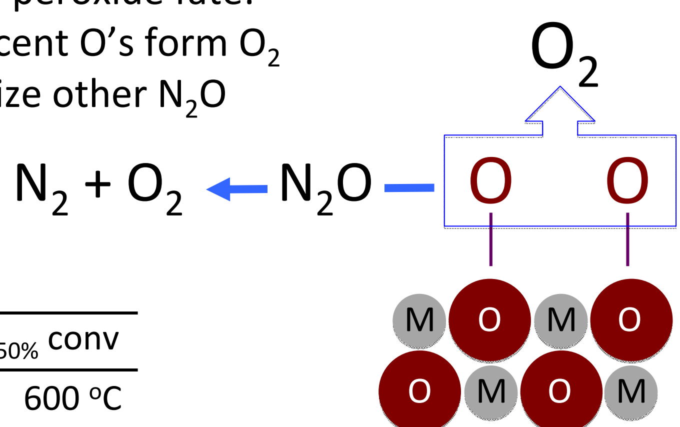
$M(O_2)$, peroxide
Sr better

Piskorz, W. et al. *J. Phys. Chem. C.* **2013** *Just Accepted* Aug. 5.

Mechanism of N_20 decomposition on MO

Surface peroxide fate:

- Adjacent O's form O_2
- Oxidize other N_2O



	$T_{50\%}$ conv
Mg	600 °C
Ca	450
Sr	530

$M(O_2)$, peroxide
Mg more mobile (close O)

Piskorz, W. et al. *J. Phys. Chem. C.* **2013** *Just Accepted* Aug. 5.

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SNCR: High temperature, no catalysts

cannot access E_A ← colder

°C
850 — 1100
optimum

hotter → NO_X oxidation competes

$[NH_3] \sim 5x[NO]$

$DeNO_x$ efficiency of NH_3 with different additives (830 °C)

- better overall conversion of NO
- lower T conversion
- less NH_3 slip

Gasnot, L.; Dao, D. Q.; Pauwels , J. F. *Energy Fuels* **2012**, *26*, 2837–2849.

SNCR: High temperature, no catalysts

DeNO$_x$ efficiency of NH_3 with different additives (830 ^oC)

additive	% NO conversion
none (NH_3 only)	42
CO	62
CH_4	47
C_2H_6	65
CH_4O	58
C_2H_6O	67

normalized for "constant C content"

OH radical production improved at low T:
$OH + NH_3 \rightarrow NH_2 + H_2O$

Then (efficient processes):
$NH_2 + NO \rightarrow NNH + OH$
$NH_2 + NO \rightarrow N_2 + H_2O$
$NNH + NH_2 \rightarrow N_2 + NH_3$

Gasnot, L.; Dao, D. Q.; Pauwels , J. F. *Energy Fuels* **2012**, *26*, 2837–2849.

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Selective catalytic oxidation (SCO) of NH_3 to N_2

$[O_2] >> [NH_3]$

Broadly applicable conversion of NH_3
- slipped from SCR
- animal waste sludge product
- byproduct of fuels derived from biomass

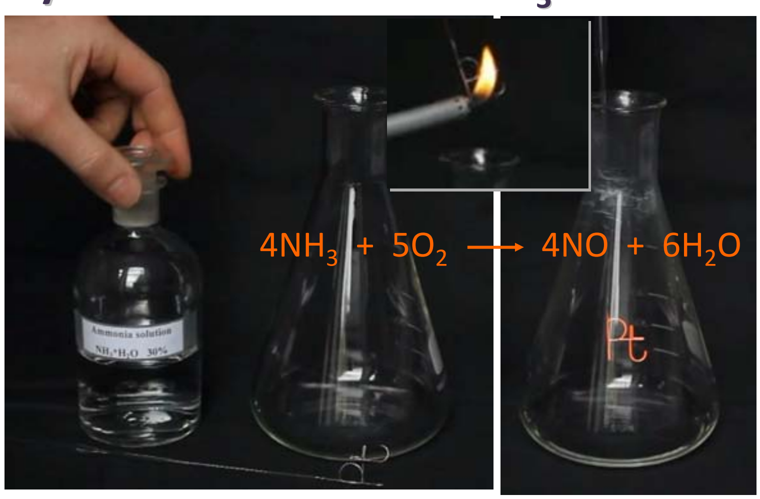
Acidic MOx excellent N_2 selectivity at moderate T (230 °C)
Lower T (< 300 °C) desired to prevent over-oxidation

Noble (Au, Pt, Pd, Rh) metals favor oxidation

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$ (Ostwald HNO_3 process)

Glassman, I.; Yetter, R. A. *Combustion, 4th ed.*; Elsevier Academic Press: Burlington, MA, 2008.
Yuan, R. –M.; Fu, G.; Xu, X.; Wan, H. –L. *J. Phys. Chem. C* **2011**, *115*, 21218–21229

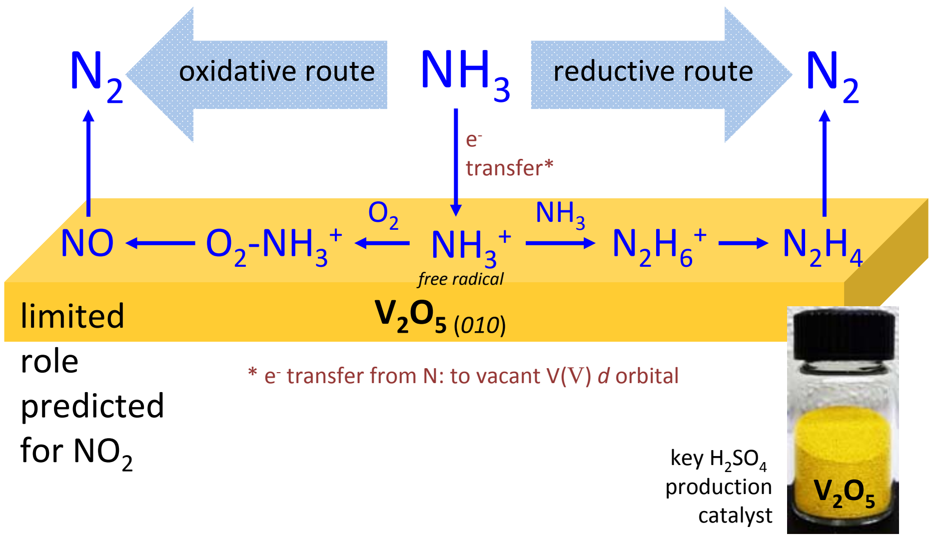
Catalytic *over*-oxidation of NH_3



Noble (Au, Pt, Pd, Rh) metals favor oxidation
(Ostwald HNO_3 process)

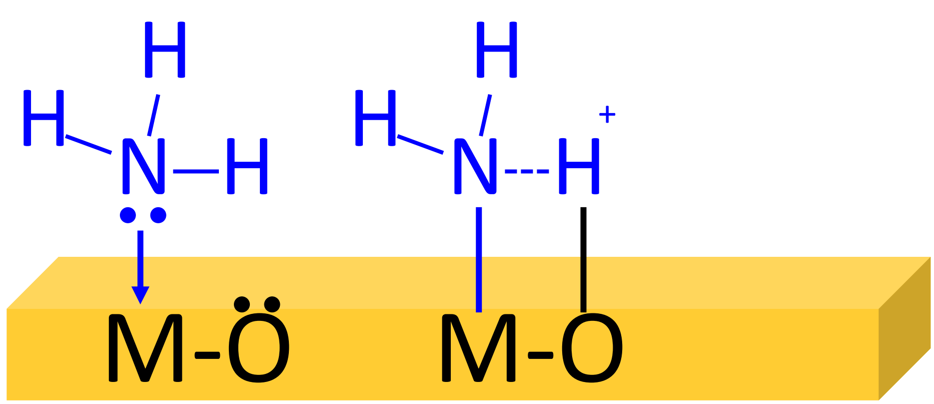
http://www.youtube.com/watch?v=ISDP-6Lv1mI

Competitive routes for NH_3 to N_2 conversion



Yuan, R. –M.; Fu, G.; Xu, X.; Wan, H. –L. *J. Phys. Chem. C* **2011**, *115*, 21218–21229

N-H activation for NH_3 on acidic metal oxide



NH_3 , N_2H_4 IP's support

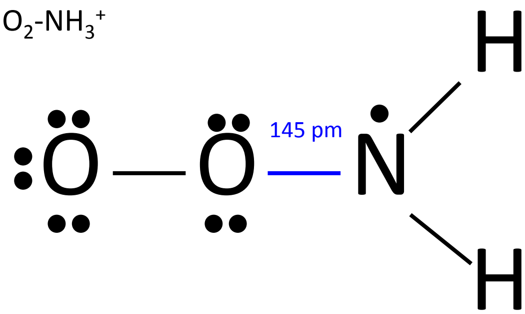
e^- transfer to V_2O_5

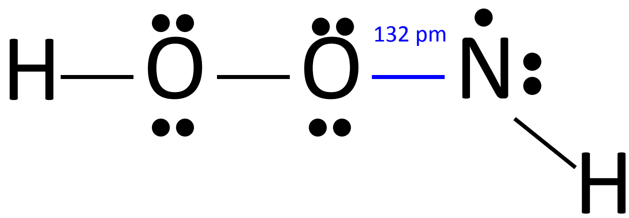
Yuan, R. –M.; Fu, G.; Xu, X.; Wan, H. –L. *J. Phys. Chem. C* **2011**, *115*, 21218–21229

Some intermediates in mechanisms

compare O_2-NH_2 with O_2-NH_3^+

plausible
O_2 reaction,
triplet
ground state





bond lengths (g) phase

Kebede, M. A.; Varner, M. E.; Scharko, N. K.; Gerber, R. B.; Raff, J. D. . *J. Am. Chem. Soc.* **2013**, *135*, 8606–8615.

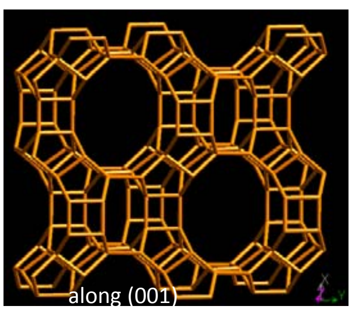
Conclusions

- M-zeolites (M = Fe, Cu) excellent SCR w/o M_{noble}
- Metal-oxides:
  - basic: NO_x traps, N_2O decomp
  - acidic: SCO, selective for N_2
- LNT + M_{noble} control N-N bond formation
- SCO (treating NH_3 slip)

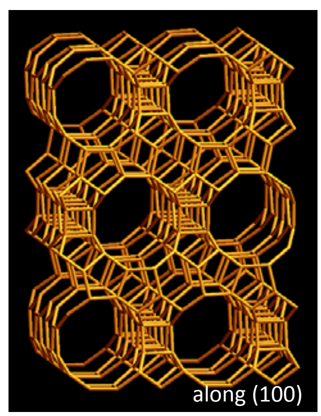
Acknowledgements:
Researchers cited
UCA Department of Chemistry

Extra slides

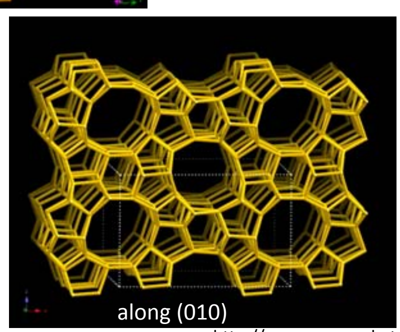
Some zeolites employed for NH_3 SCR



MOR



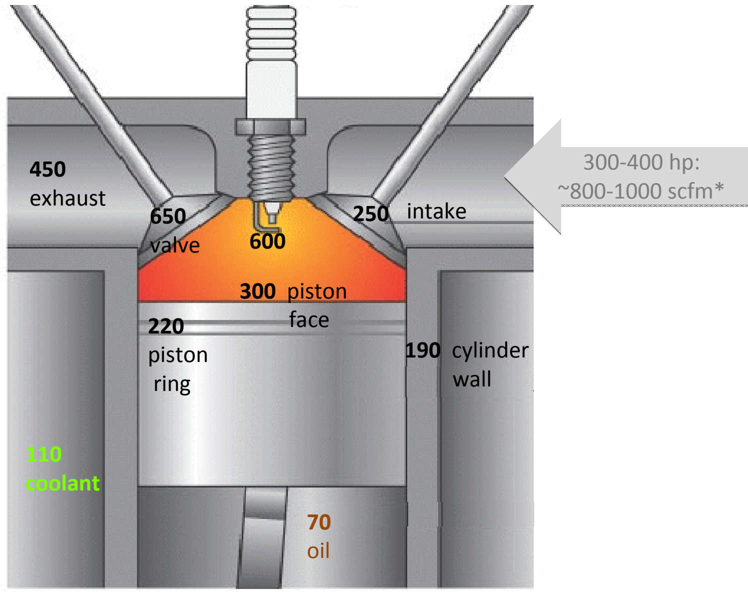
BEA



ZSM-5

http://www.iza-structure.org/databases/
http://www.personal.utulsa.edu/~geoffrey-price/zeolite/index.html

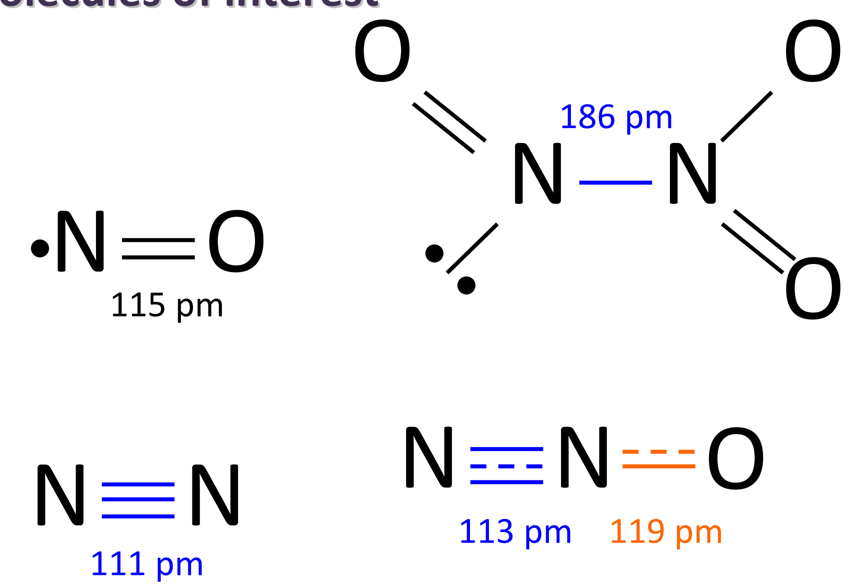
Engine component temperatures (°C)[§]



[§]F. Salazar, U. Notre. Dame, Apr. 1998

*Johnson *et al. Environ. Sci. Technol.* **2009**, *43*, 3959–3963

Molecules of interest



Exhaust gas from M85 engines

NO > NO_2 >> N_2O, other NO_x

TABLE 1: Raw M85 Exhaust @ 100 seconds, Post-Cat

Component	Conc (ppm)	Error (±)
H_2O	143577.25	4476.26
CO	166.42	10.55
CO_2	122191.26	1803.23
NO	127.23	9.84
NO_2	1.59	8.68
N_2O	6.7	1.82
NH_3	25.39	0.54
CH_4	21.02	2.71
C_2H_2	0	4.08
C_2H_4	0.63	0.7
C_2H_6	0.64	3.05
C_3H_6	0	2.44
H_2CO	39.17	1.65
CH_3OH	138.88	2.79
13BUT	1.85	1.62
ISBUT	0	1.35
HCONT	1.18	1.74

The Use of FT-IR to Analyze NOx Gases in Automobile Exhaust App. Note 50649 Thermo Sci. 2007.

NO_2^- suppresses N_2O formation in sludge

$$NH_3 \longrightarrow NH_2OH \longrightarrow NO_2^-$$

N_2O can be a byproduct

low NO_2^- (20 – 25 mg N / L) enhances N_2O production

high NO_2^- (200 – 250 mg N / L) suppresses N_2O production

Bacterial pathways change with increased DO

*ammonia oxidizing bacteria
aerated sludge

Law, Y.; Lant, P.; Yuan, Z. *Environ. Sci. Technol.*, **2013**, *47* (13), pp 7186–7194

Standard SCR mechanism

Standard	$4NH_3$-cat + $4NO$ + O_2 → $4N_2$ + $6H_2O$
Fast	$2NH_3$-cat + NO + NO_2 → $2N_2$ + $3H_2O$
Slow	$4NH_3$-cat + $3NO_2$ → $3.5N_2$ + $6H_2O$

reactions: 2/3 of N_2O were activated by $N_2O \rightarrow NO + N$ (a) and 1/3 by $N_2O \rightarrow N_2 + O$ (b), and the formed NO and O_2 react with NH_3 following a typical SCR mechanism ($NO + NH_3 + (1/4)O_2 \rightarrow N_2 + (3/2)H_2O$).

$$NH_3 + OH \rightarrow NH_2 + H_2O \quad (R7)$$

$$N_2O \rightarrow N_2 + O \quad (R1)$$

$$2N_2O \rightarrow 2NO + N_2 \quad (R6)$$

$$NH_2 + NO \rightarrow NH_2NO \rightarrow N_2 + OH_2 \quad (R14)$$

$$NO + O \rightarrow NO_2 \quad (R11)$$

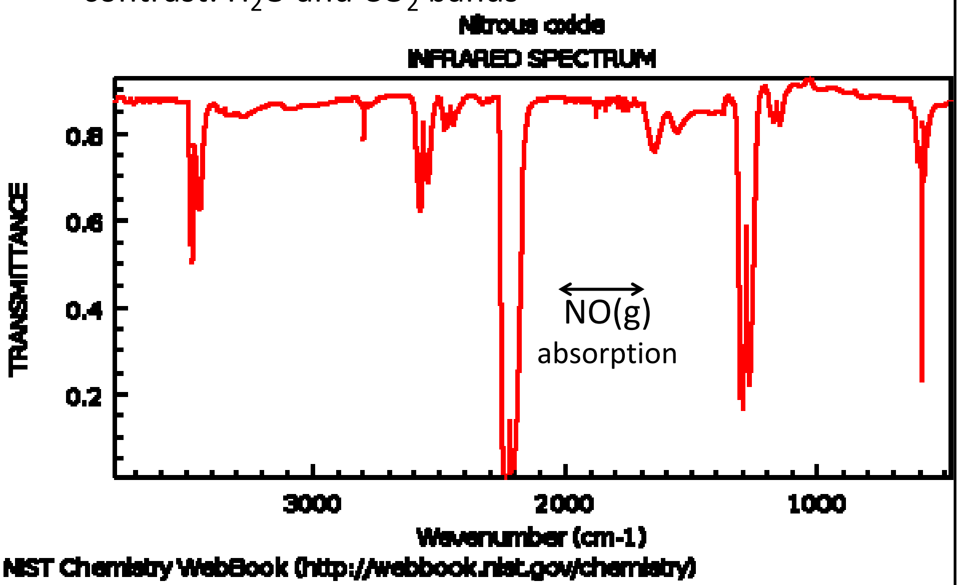
$$O^{2-} + 2NO_2 \leftrightarrow NO_2^- + NO_3^- \quad (R15)$$

$$NH_4^+ + NO_2^- \rightarrow NH_4NO_2 \rightarrow NH_2NO + H_2O \rightarrow N_2 + H_2O \quad (R16)$$

Zhang, X.; Shen, S.; He, C.; Ma, C.; Cheng, J.; Li, L.; Hao, Z. *ACS Catal.* **2012**, *2*, 512–520

N_2O absorption spectrum

contrast: H_2O and CO_2 bands



NO absorption spectrum

contrast: H_2O and CO_2 bands