Isotopic studies of NO_x reduction over Pt-Ba/Al_2O_3 LNT catalyst

Laboratory of Catalysis and Catalytic Processes LCCP

L. Righini, N. Artioli, L. Castoldi, L. Lietti*, P. Forzatti

Laboratory of Catalysis and Catalytic Processes LCCP Energy Department, Politecnico di Milano

*luca.lietti@polimi.it

Lean NO_x Traps (LNTs): pathways in the reduction of stored NO_x

• Mechanistic aspects of the reduction of stored NO_x are still under debate. *Possible steps:*

Stored NO_x

surface diffusion / spillover of stored NOx towards Pt

release of NO / formation of NO-related intermediates

reduction of NO / NO-related intermediates over Pt

N_2, N_2O, NH_3

Clayton et al., Appl. Catal. B, 90 (2009) 662
Kabin et al., Catal. Today, 96 (2004) 79
Lietti et al., J. Catal., 257 (2008) 270;
L.Cumaranatunge et al., J. Catal. 2007,
J.A. Pihl et al., SAE Paper 01-3441 (2006)

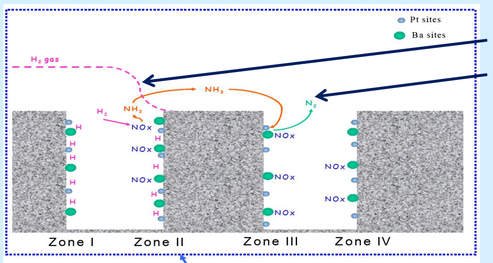
Possible driving force of NO_x release:

- heat of reductant combustion reactions (THERMAL RELEASE)
- decrease of equilibrium stability of NO_x due to decrease of P_{O2} and P_{NO} (THERMODYNAMIC RELEASE)
- establishment of net reducing environment (CHEMICAL RELEASE)

• Open issues: Pathways of NO_x release and subsequent reduction can be hardly decoupled

^{15}NO/NO Isotopic exchange technique has been used to investigate independently the two steps

Pathways in the reduction of stored NO_x by H_2 (H_2 front model):



Step 1: $Ba(NO_3)_2 + 8\ H_2 \rightarrow 2\ NH_3 + Ba(OH)_2 + 4\ H_2O$

Step 2: $3\ Ba(NO_3)_2 + 10\ NH_3 \rightarrow 8\ N_2 + 3\ Ba(OH)_2 + 12\ H_2O$

Steps 1 + 2 : $Ba(NO_3)_2 + 5\ H_2 \rightarrow Ba(OH)_2 + N_2 + 4\ H_2O$

Step 1 is faster than step 2

• Reactivity of NH_3 with stored NO_x is RDS in the formation of N_2

Reactivity of NH_3 with nitrates, nitrites, gas phase NO has been investigated by using ^{15}NO

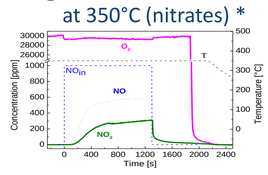
Methods

• Catalysts: Pt-Ba/Al_2O_3 (Pt=1% w/w; Ba=16% w/w) and Ba/Al_2O_3 (Ba=16% w/w) prepared by incipient wetness impregnation of commercial γ-Al_2O_3 calcined at 700°C

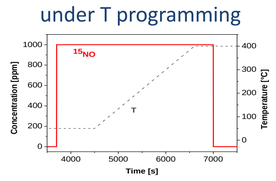
• $^{15}NO/^{14}NO$ Isotopic Exchange experiments with stored $^{14}NO_x$

$^{14}NO_x$ storage

$^{14}NO/O_2$ adsorption at 150°C (nitrites), at 350°C (nitrates) *



Exposure to ^{15}NO under T programming

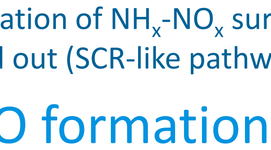


* : In the case of Ba/Al_2O_3: $^{14}NO_2$ adsorption at 350°C

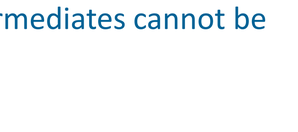
• Reactivity of NH_3 with adsorbed $^{15}NO_x$ (nitrites, nitrates)

$^{15}NO_x$ storage

$^{15}NO/O_2$ adsorption at 150°C (^{15}nitrites), at 350°C (^{15}nitrates)



Exposure to NH_3 under T programming

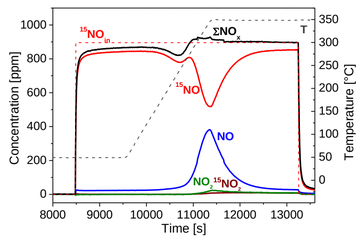


• Reactivity of NH_3 with gas-phase ^{15}NO (Exposure to NH_3 +^{15}NO under T programming)

^{15}NO/NO isotopic exchange

PtBa/Al_2O_3 Heating from 50°C in ^{15}NO after NO/O_2 adsorption at 350°C

Nitrates

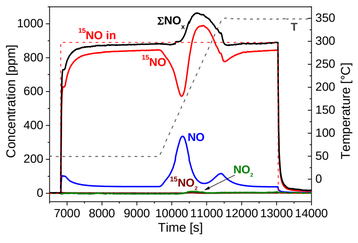


• $^{15}NO/^{14}NO$ exchange from 200-250 °C, i.e. below T_{ADS} & T_{DEC} (~320°C)

$Ba(^{14}NO_3)_2 + 2\ ^{15}NO \rightarrow Ba(^{15}NO_3)_2 + 2\ ^{14}NO$

PtBa/Al_2O_3 Heating from 50°C in ^{15}NO after NO/O_2 adsorption at 150°C

Nitrites



• $^{15}NO/^{14}NO$ exchange observed already at 50°C, well below T_{ADS} & T_{DEC} (~125°C)

• at 250°C almost complete exchange reached

$Ba(^{14}NO_2)_2 + 2\ ^{15}NO \rightarrow Ba(^{15}NO_2)_2 + 2\ ^{14}NO$

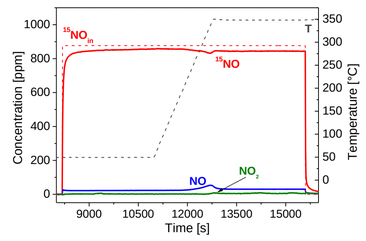
- *the $^{15}NO/^{14}NO$ exchange occurs at $T < T_{ADS}$ & T_{DEC}*
- *nitrites are more readily exchanged than nitrates*

Pt role

Pt role in isotopic exchange

Ba/Al_2O_3 Heating from 50°C in ^{15}NO after NO_2 adsorption at 350°C

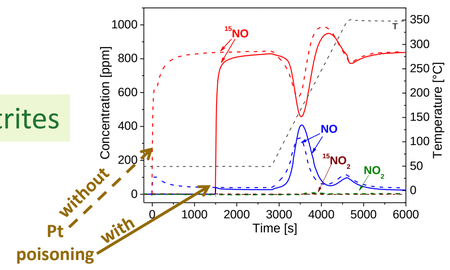
Nitrates



• the $^{15}NO/^{14}NO$ exchange does not occur in the absence of Pt

PtBa/Al_2O_3 Heating from 50°C in ^{15}NO after NO/O_2 adsorption at 150°C with subsequent Pt poisoning under CO exposure at RT

Nitrites



After CO poisoning, $^{15}NO/^{14}NO$ exchange:

• at 50°C is almost negligible

• up to 160°C occurs at lower rate

- *the $^{15}NO/^{14}NO$ exchange is a Pt catalyzed reaction*

Conclusive remarks

According to one mechanism, stored NO_x are released at Pt sites, possibly with formation of NO or NO-related intermediates, thus reduced to the reaction products (N_2, N_2O, NH_3).

NO_x release

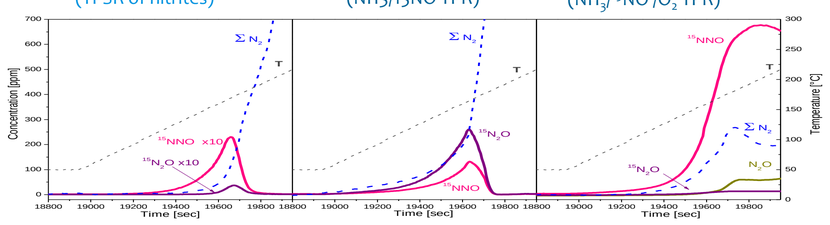
- The NO_x release is a Pt-catalyzed reaction, not thermally driven, as pointed out by TPIE experiments.
- It involves the spillover of NO_x towards Pt with subsequent decomposition, whose rate limiting factor is the removal of O from Pt
- reduced Pt sites is the driving force for the onset of the reduction process
- the release of NO_x is the RDS in the regeneration process.

N_2 formation

- N_2 formation occurs by a statistical recombination at the Pt sites of N ad-atoms formed upon NO and NH_3 decomposition. Due to the relative abundance of $^{15}N^{14}N$, formation of NH_x-NO_x surface intermediates cannot be ruled out (SCR-like pathway)

N_2O formation

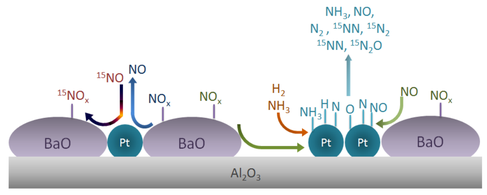
NH_3+^{15}nitrites (TPSR of nitrites) | NH_3+^{15}NO (NH_3/^{15}NO TPR) | NH_3+^{15}NO+O_2 (NH_3/^{15}NO /O_2 TPR)



- Only labelled N_2O molecules detected and produced by the reaction between undissociated ^{15}NO with N-adatoms:

$$^{15}NO_{ads} + N_{ads} \rightarrow {}^{15}NNO$$
$$^{15}NO_{ads} + {}^{15}N_{ads} \rightarrow {}^{15}N_2O$$

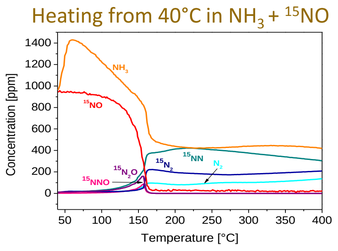
- N_2O formation is favoured by high NO concentration (TPR) and by the presence of oxidized Pt sites (low T, O_2 presence)
- reduction of nitrites leads to a higher N_2O formation than nitrates due to their easier NO release



Reaction of NH_3 with gaseous NO and stored NO_x ($PtBa/Al_2O_3$)

NH_3 + ^{15}NO

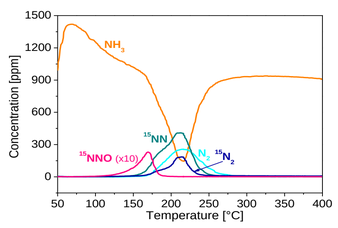
Heating from 40°C in NH_3 + ^{15}NO



- initial formation of only labeled N_2O then and all types of N_2; complete selectivity to N_2 above 180°C
- isotopic distribution in line with the statistical recombination of N ad-atoms formed by NO and NH_3 dissociation

NH_3 + ^{15}nitrites

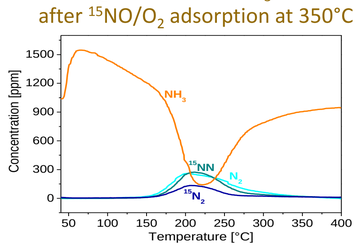
Heating from 40°C in NH_3 after $^{15}NO/O_2$ adsorption at 150°C



- minor initial formation of $^{15}N_2O$
- formation of all nitrogen isotopes, abundance of single-labelled $^{14}N^{15}N$
- the presence of $^{15}N_2$ and of $^{14}N_2$ indicates the self-coupling of N-atoms of the stored nitrites and of ammonia

NH_3 + ^{15}nitrates

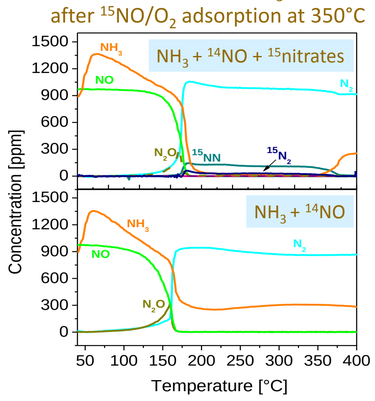
Heating from 40°C in NH_3 after $^{15}NO/O_2$ adsorption at 350°C



- reaction occurs from 150°C
- complete selectivity to N_2 (only trace amounts of N_2O)
- formation of all N_2 isotopes, with abundance of unlabelled N_2 and $^{14}N^{15}N$

NH_3 + ^{14}NO + ^{15}nitrates

Heating from 40°C in NH_3+^{14}NO after $^{15}NO/O_2$ adsorption at 350°C



- initial formation of unlabeled N_2O and N_2 (involvement of gas-phase NO)
- @ T > 180°C complete NH_3 consumption and evolution of N_2: limited formation of ^{15}N-containing species due to the faster reaction of NH_3 with gaseous NO
- Higher reactivity of NO if compared to nitrates

- *N_2 is formed upon statistical recombination of N ad-atom coming from NO and NH_3 dissociation over Pt sites*
- *the SCR-like pathway (coupling of NO- and NH_3-derived intermediates) can occur, explaining the ^{15}NN abundance*
- *the NO release is the rate determining step of the reduction process*