The beneficial effect of SO_2 on platinum migration and NO oxidation over diesel oxidation catalysts

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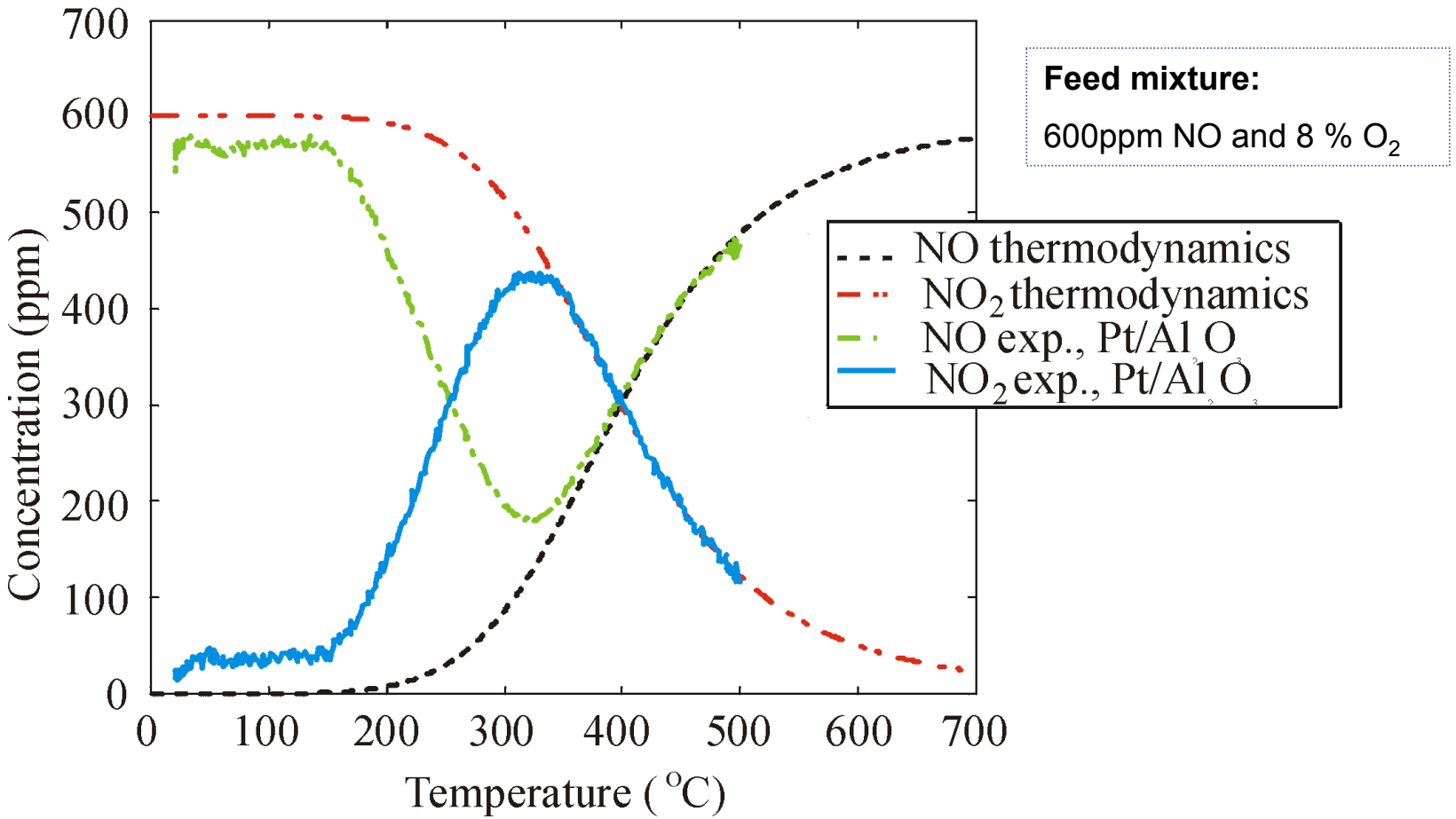
Outline

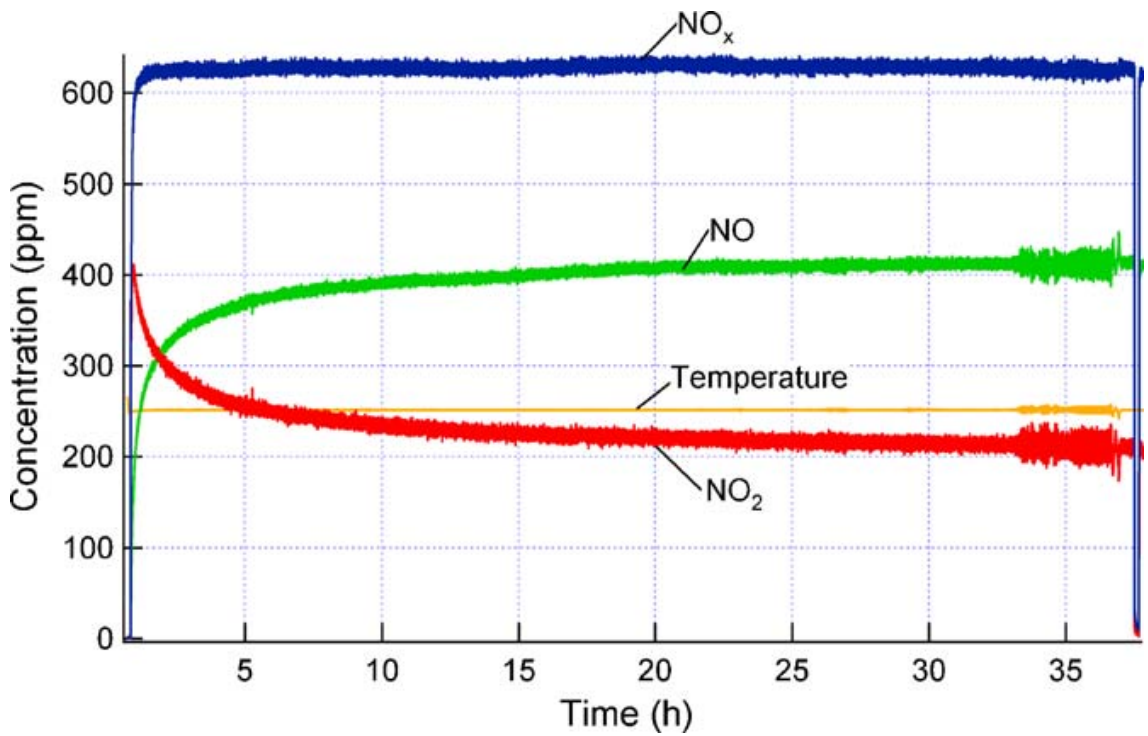
- NO oxidation on Pt/Al_2O_3
- Platinum oxide formation
- Effect of support on NO oxidation
- Effect of water on NO oxidation
- Effect of propene on NO oxidation
- Beneficial effects of SO_2 pre-treatment on NO oxidation
- Conclusions
- Acknowledgements

NO oxidation on Pt/Al_2O_3



L. Olsson, B. Westerberg, H. Persson, E. Fridell, M. Skoglundh, B. Andersson, *J. Phys. Chem. B*, 103 (1999) 10433

NO oxidation over Pt/Al_2O_3



Pretreatment:

0.1% H_2/Ar at 400°C for 10 min with, followed by 10 min Ar

Feed mixture:

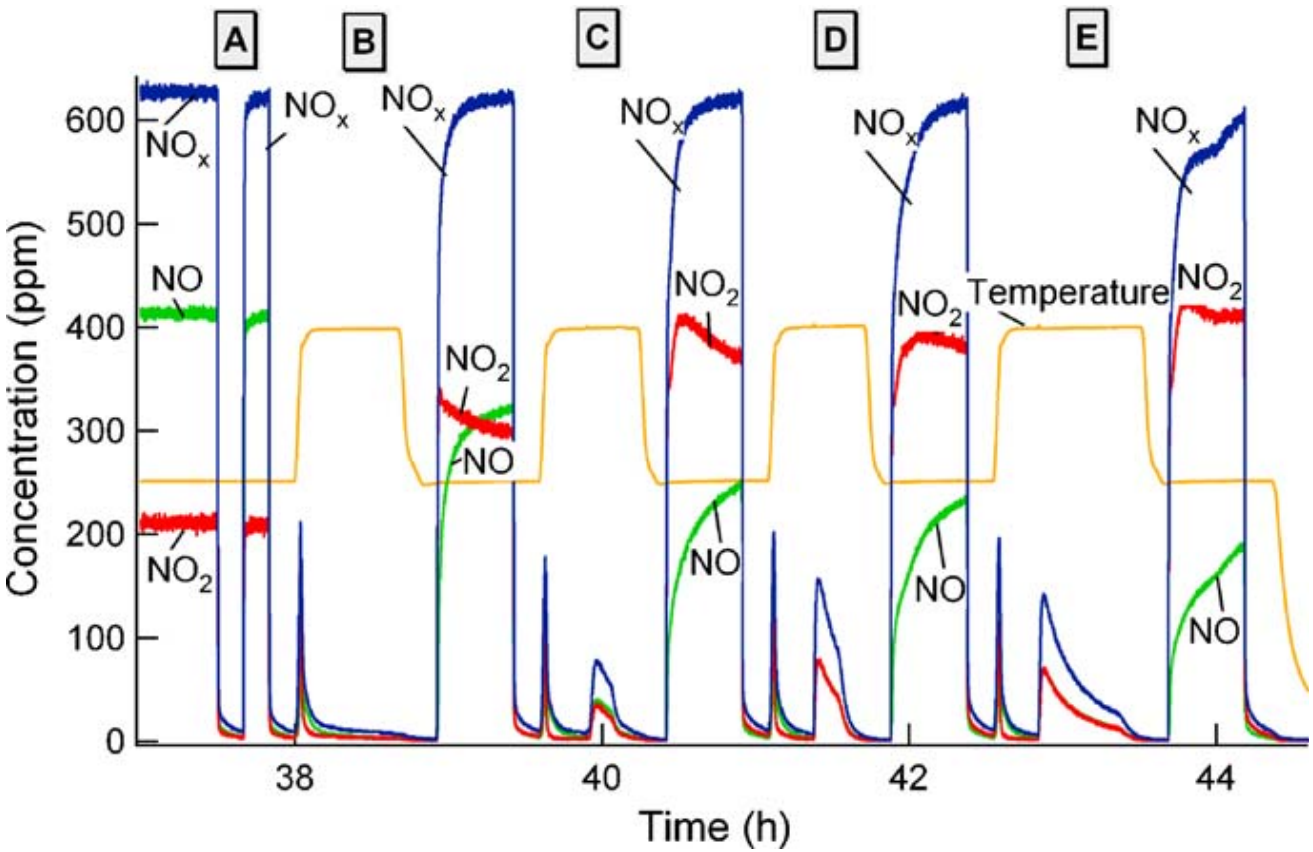
630ppm NO and 8 % O_2, for 36 h.

Temperature: 250°C

SV: 39 000 h^{-1}

L. Olsson and H. Karlsson, *Catalysis Today* 147S (2009) S290.

Removal of platinum oxides



Feed mixture:

A)10min Ar at 250°C

(B) 30min Ar at 400°C

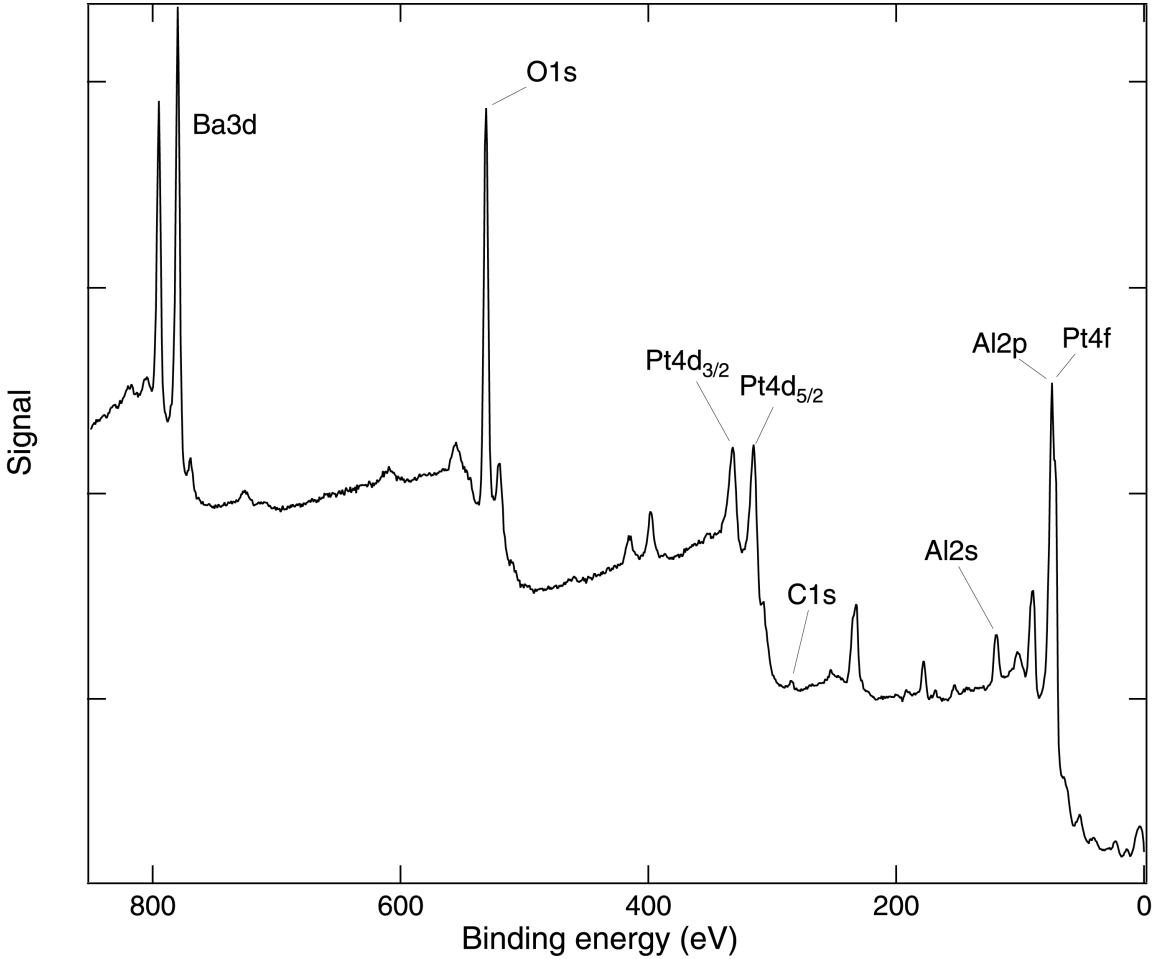
(C) 10min 550ppm C_3H_6 at 400°C

(D)10min 0.1%H_2 at 400°C

(E) 30min1%H_2 at 400°C

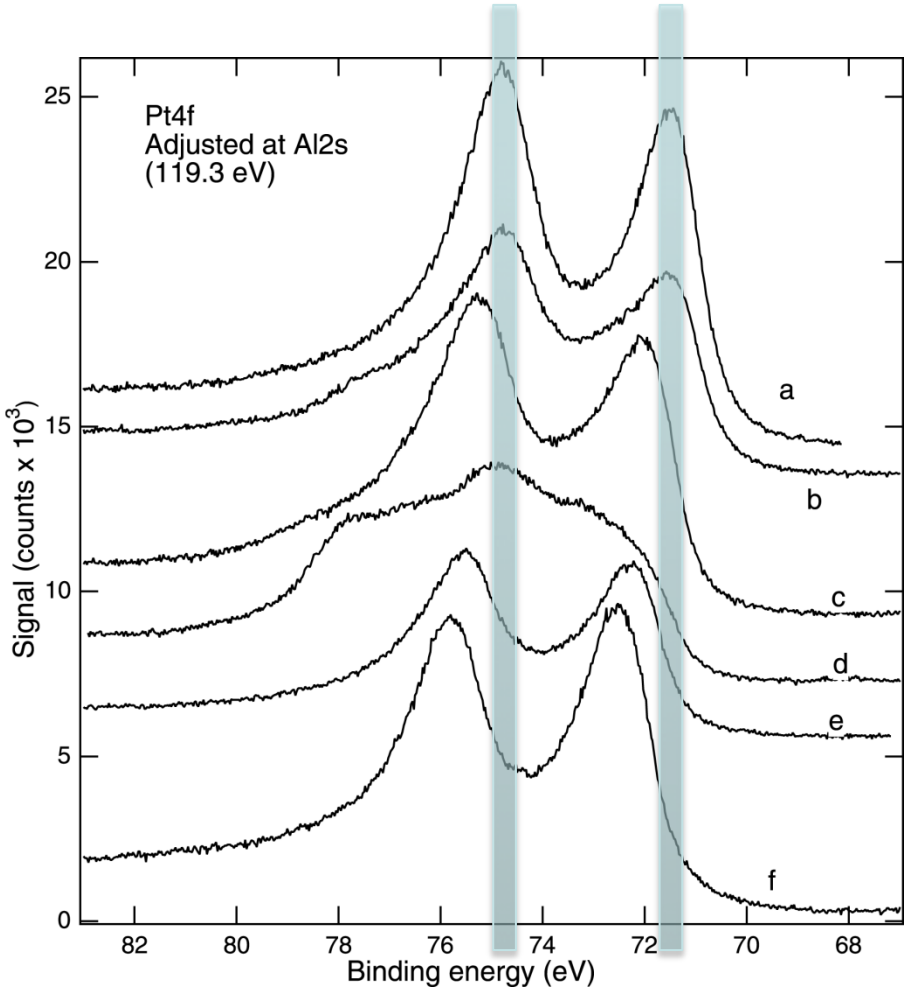
L. Olsson and H. Karlsson, *Catalysis Today* 147S (2009) S290.

XPS spectra of $Pt/BaO/Al_2O_3$



L. Olsson and E. Fridell, J. of Catalysis 2002, 210, 340.

XPS Pt4f spectra for different pre-treatments



a) Pt/Al_2O_3, H_2

b) $Pt/BaO/Al_2O_3$, H_2

c) Pt/Al_2O_3, NO_2

d) $Pt/BaO/Al_2O_3$, NO_2

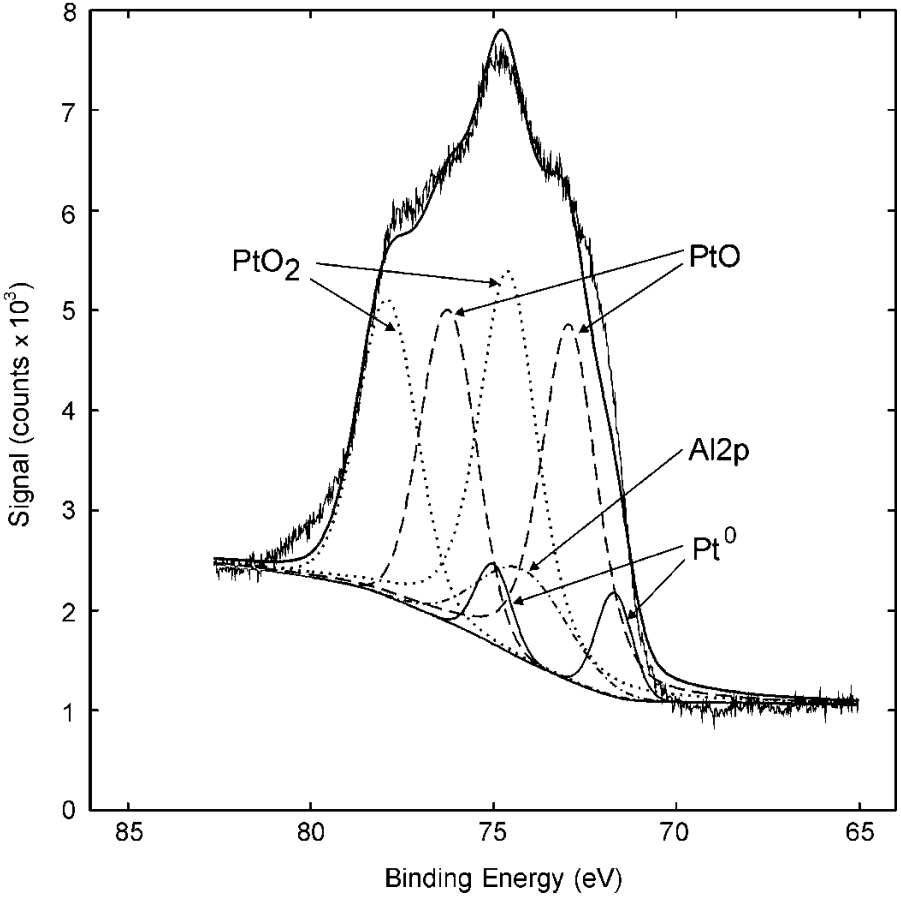
e) Pt/Al_2O_3, O_2

f) $Pt/BaO/Al_2O_3$, O_2

L. Olsson and E. Fridell, J. of Catalysis 2002, 210, 340.

XPS Pt4f spectra deconvolution

$Pt/BaO/Al_2O_3$, NO_2



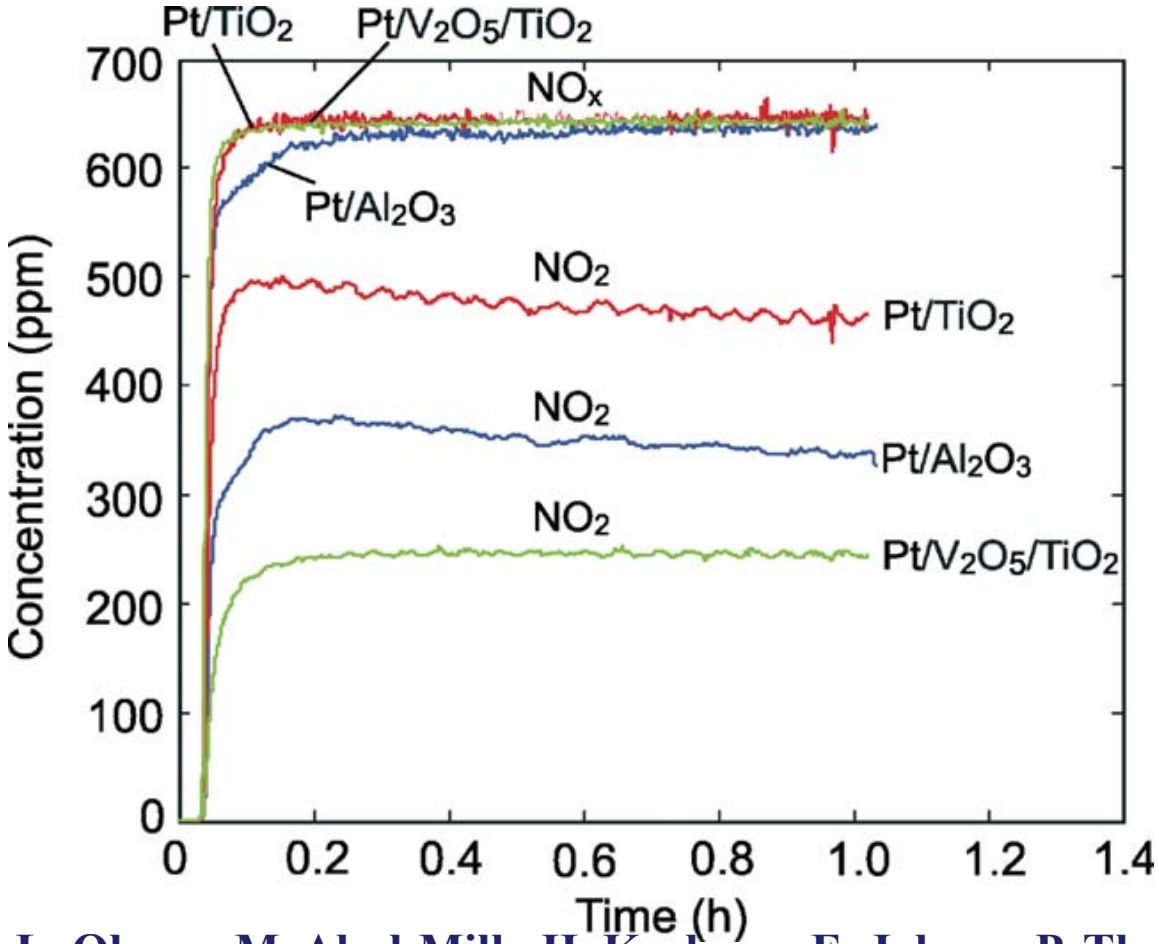
L. Olsson and E. Fridell, J. of Catalysis 2002, 210, 340.

Effect of support on NO oxidation

Catalyst	Al_2O_3 or TiO_2 (mg)	V_2O_5 (mg)	Pt (mg)	BET (m^2/g monolith)	Dispersion CO/Pt
Pt/Al_2O_3	827	-	15.4	133	0.29; 0.30; 0.30
Pt/TiO_2	857	-	17.5	77	0.08; 0.07; 0.07; 0.08
$Pt/V_2O_5/TiO_2$	807	40	17.6	68	-

L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormählen and A. Hinz, *Topics in Catalysis 30/31* (2004) 85.

Effect of support on NO oxidation



Feed mixture:

630ppm NO and 8 % O_2

Temperature: 200°C

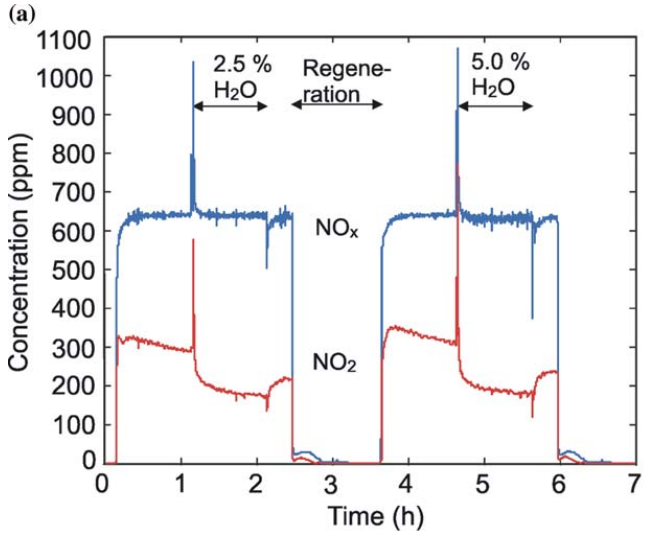
SV= 39 000 h^{-1}

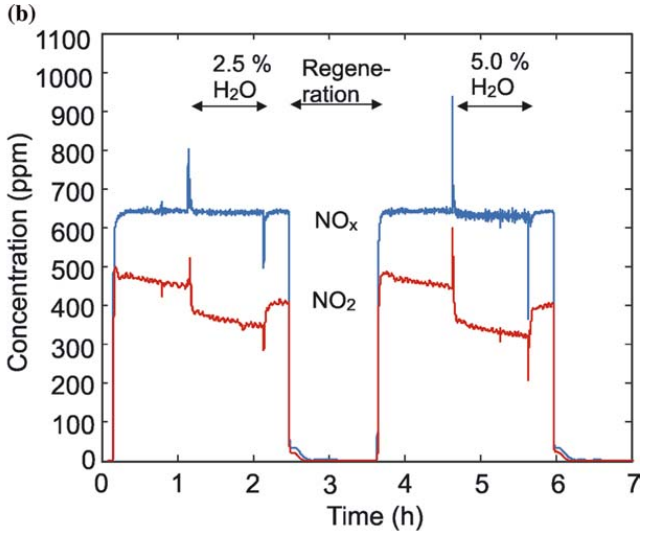
L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormählen and A. Hinz, *Topics in Catalysis 30/31* (2004) 85.

Effect of support on NO oxidation

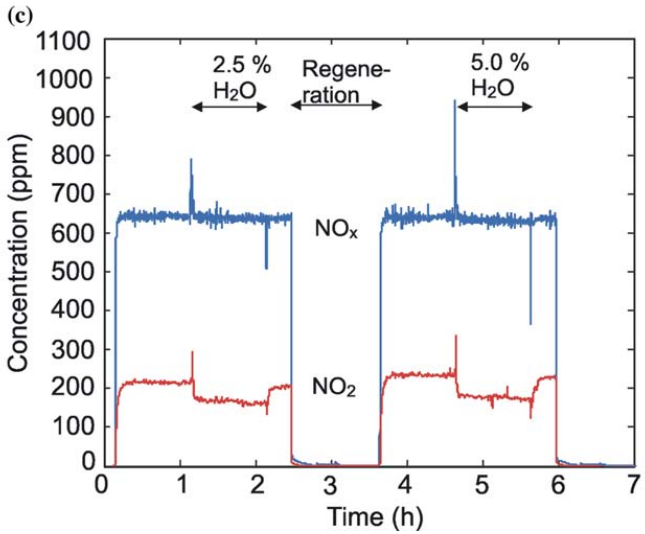
- Influence of water at 200°C

Pt/Al_2O_3





Pt/TiO_2



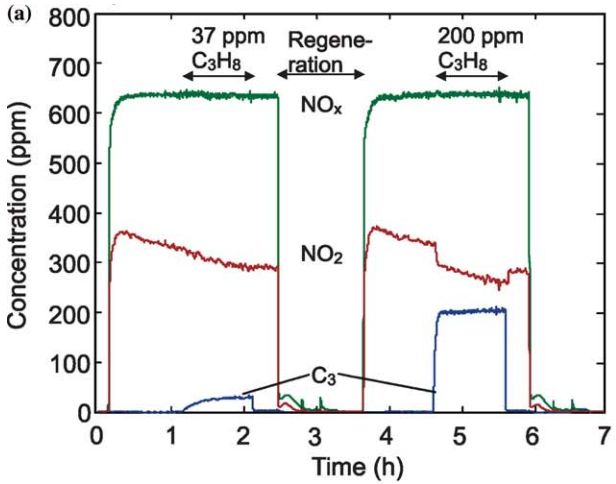
$Pt/V_2O_5/TiO_2$

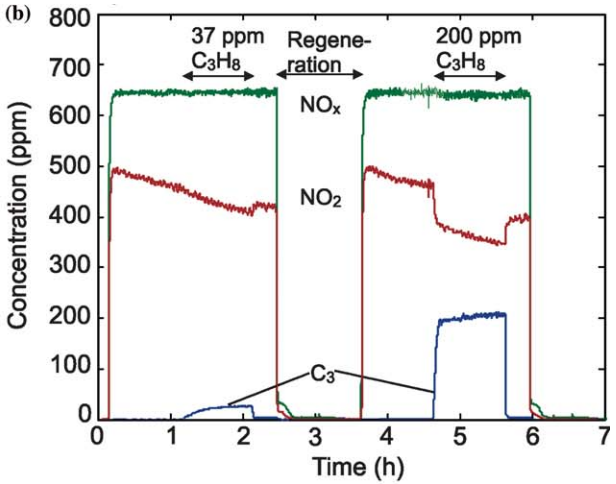
L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormählen and A. Hinz, *Topics in Catalysis 30/31* (2004) 85.

Effect of support on NO oxidation

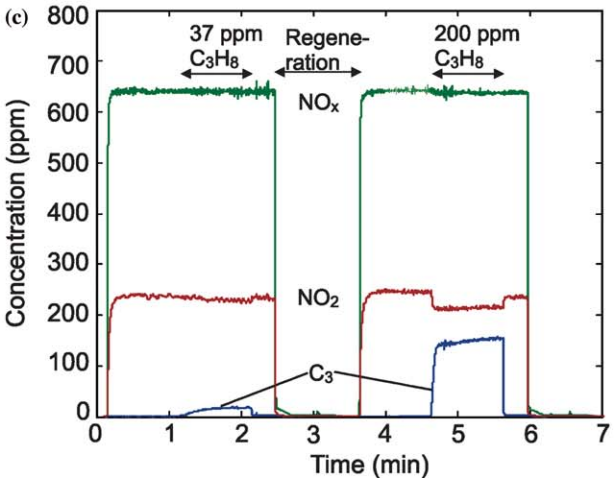
- Influence of C_3H_6 at 200°C

Pt/Al_2O_3





Pt/TiO_2



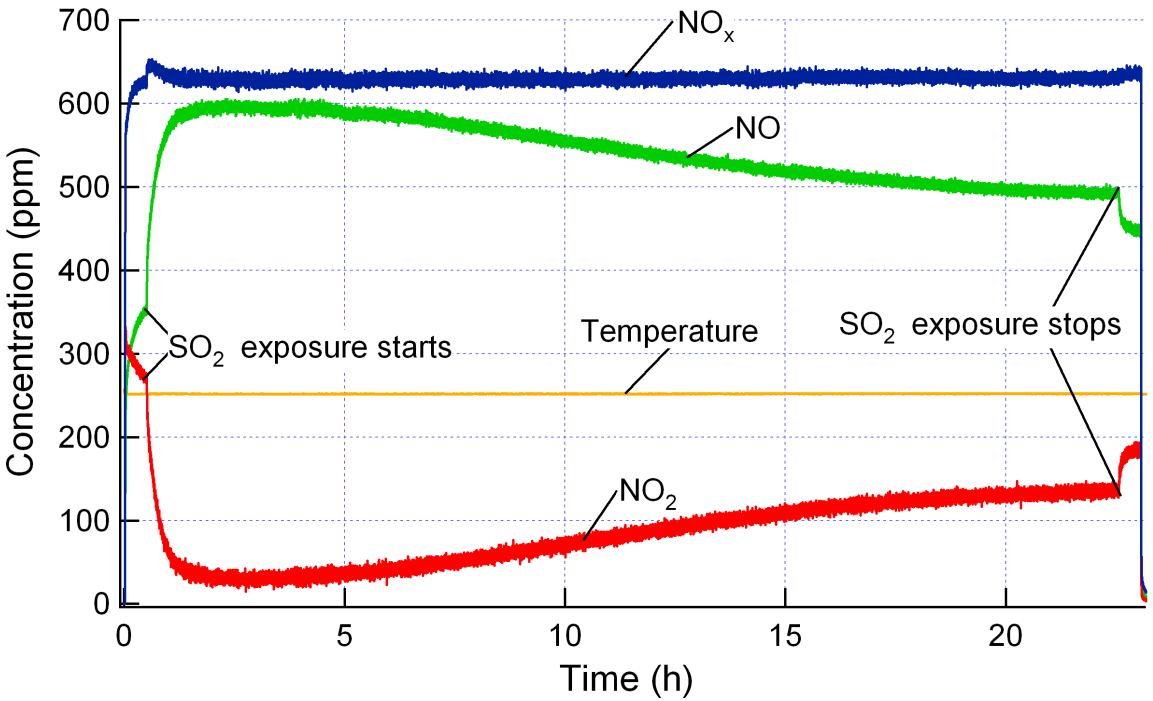
$Pt/V_2O_5/TiO_2$

L. Olsson, M. Abul-Milh, H. Karlsson, E. Jobson, P. Thormählen and A. Hinz, *Topics in Catalysis 30/31* (2004) 85.

Experimental conditions for sulphur influence of NO oxidation on Pt/Al_2O_3

1. Degreening: 2% H_2 for 30 min at 400°C, 45 min at 650°C in Ar
2. Measure platinum dispersion with CO TPD
3. NO oxidation exp.
   - (i): 1% H_2/Ar at 400°C for 30 min (pretreatment)
   - (ii) 10 min Ar at 400°C
   - (iii) 630ppmNO+8%O_2 for 35 min at 40°C
   - (iv) Temperature ramp with a rate of 5°C/min up to 400°C
4. Long NO oxidation+SO_2 exp.
   - (i): 1% H_2/Ar at 400°C for 30 min (pretreatment)
   - (ii) 10 min Ar at 400°C, cool to 250°C
   - (iii) 250°C: 630ppmNO+8%O_2 for 30 min at 250°C
   - (iv) 250°C: 630ppmNO+8%O2+30ppm SO_2 for 22h
   - (v) 250°C: 630ppmNO+8%O2 for 30 min
5. NO oxidation exp.
6. Measure platinum dispersion with CO TPD

Influence of SO_2 on NO oxidation over Pt/Al_2O_3 at 250°C



Feed mixture:

630ppm NO and 8 % O_2, for 23 h.

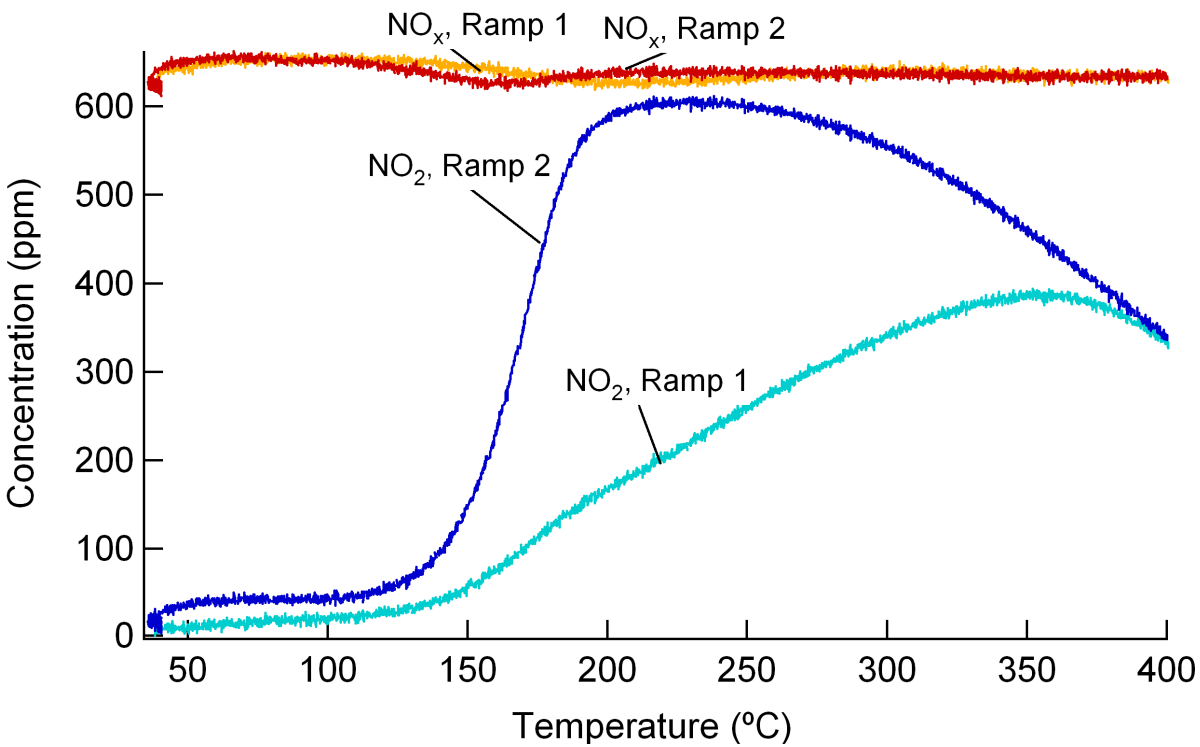
After 30 min was 30 ppm SO_2 added and it was removed after 22.5h.

Temperature: 250°C

SV= 39 000 h^{-1}

L. Olsson and H. Karlsson, *Catalysis Today* 147S (2009) S290.

Influence of SO_2 on NO oxidation on Pt/Al_2O_3



Feed mixture:

630ppm NO and 8 % O_2,

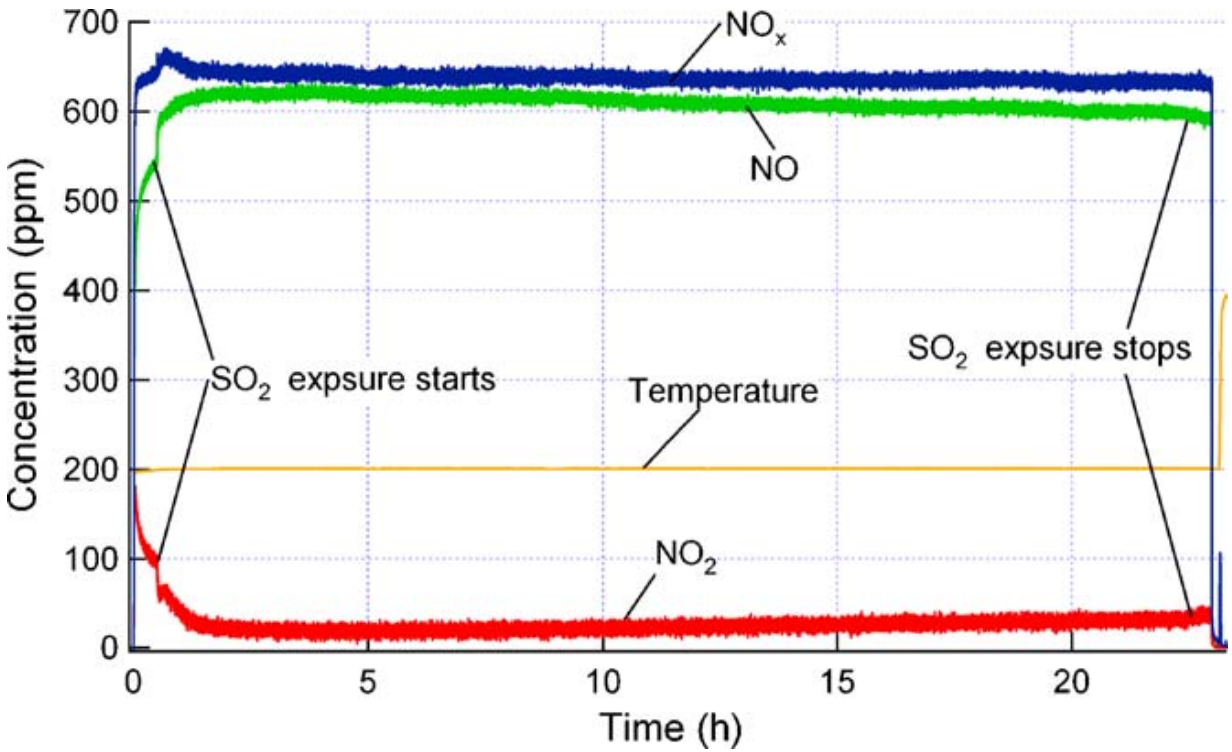
5 °C/min

SV= 39 000 h^{-1}

- Dispersion before SO_2 exposure: 12%
- Dispersion before SO_2 exposure: 3.5%

L. Olsson and H. Karlsson, *Catalysis Today* 147S (2009) S290.

Influence of SO_2 on NO oxidation over Pt/Al_2O_3 at 200°C



Feed mixture:

630ppm NO and 8 % O_2, for 23 h.

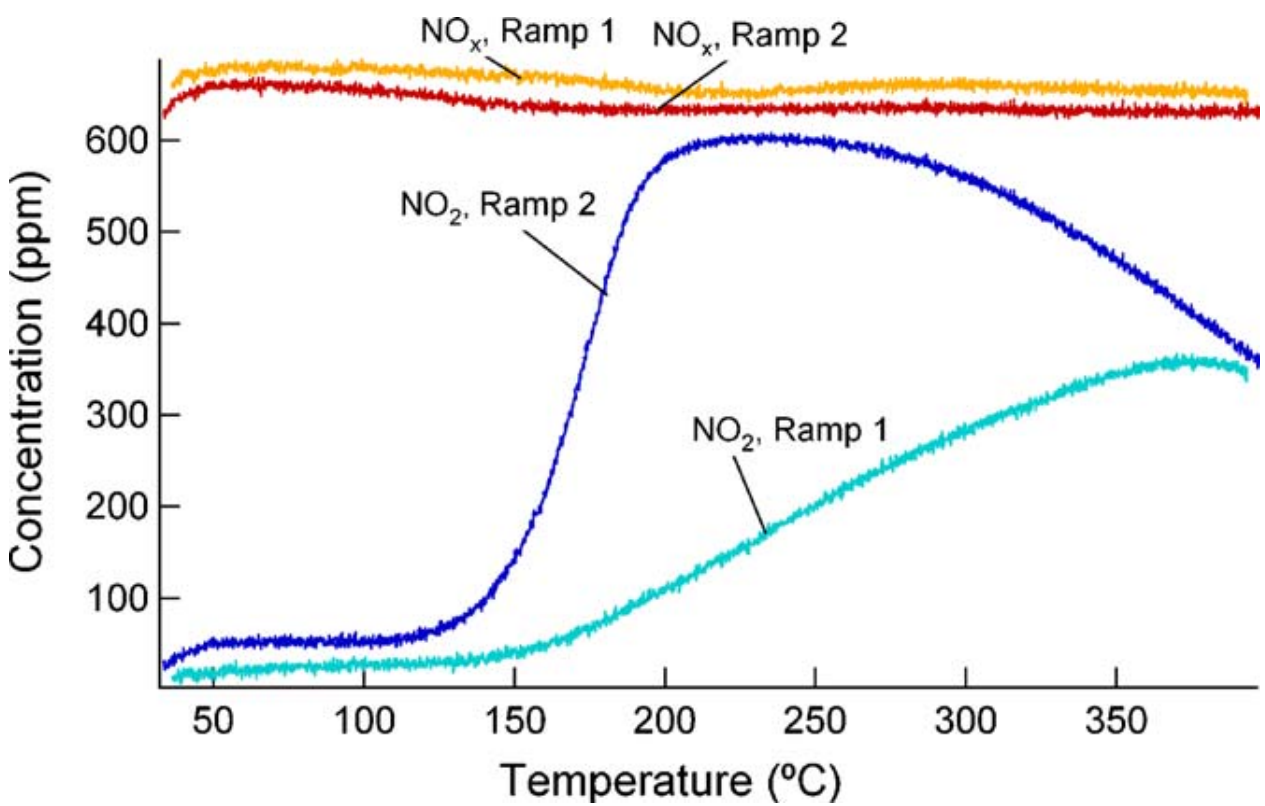
After 30 min was 30 ppm SO_2 added and it was removed after 22.5h.

Temperature: 200°C

SV= 39 000 h^{-1}

L. Olsson and H. Karlsson, *Catalysis Today* 147S (2009) S290.

Influence of SO_2 on NO oxidation on Pt/Al_2O_3



Feed mixture:

630ppm NO and 8 % O_2,

5 °C/min

SV= 39 000 h^{-1}

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Conclusions

- NO oxidation decreases with time over Pt/Al_2O_3, due to formation of platinum oxides
- XPS showed platinum oxide formation
- Increase platinum oxide formation when barium is present, due to that it is alkaline
- The addition of vanadia to Pt/TiO_2, made the catalyst more stable. Although with a lower activity. Vanadia is acidic.
- SO_2 initially deactivates the NO oxidation on Pt/Al_2O_3
- After about 2h with $NO+O_2+SO_2$, the activity slowly increases
- After 22h of $NO+O_2+SO_2$ exposure at 250°C, the catalyst was regenerated and NO oxidation activity increased significantly.
- The Pt dispersion had decreased from 12 to 3.5%
- SO_2 induces Pt sintering already at 200 and 250°C

Acknowledgements

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