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$_2$O$_3$
• 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$_2$O$_3$

Feed mixture: 600 ppm NO and 8% O$_2$

NO oxidation over Pt/Al₂O₃

Pretreatment:
0.1% H₂/Ar at 400°C for 10 min with, followed by 10 min Ar

Feed mixture:
630ppm NO and 8% O₂, for 36 h.

Temperature: 250°C
SV: 39 000 h⁻¹
Removal of platinum oxides

Feed mixture:
A) 10 min Ar at 250°C
(B) 30 min Ar at 400°C
(C) 10 min 550 ppm C₃H₆ at 400°C
(D) 10 min 0.1% H₂ at 400°C
(E) 30 min 1% H₂ at 400°C

XPS spectra of Pt/BaO/Al$_2$O$_3$

XPS Pt4f spectra for different pre-treatments

a) Pt/Al$_2$O$_3$, H$_2$

b) Pt/BaO/Al$_2$O$_3$, H$_2$

c) Pt/Al$_2$O$_3$, NO$_2$

d) Pt/BaO/Al$_2$O$_3$, NO$_2$

e) Pt/Al$_2$O$_3$, O$_2$

f) Pt/BaO/Al$_2$O$_3$, O$_2$

XPS Pt4f spectra deconvolution

Pt/BaO/Al₂O₃, NO₂


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Effect of support on NO oxidation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{Al}_2\text{O}_3$ or $\text{TiO}_2$ (mg)</th>
<th>$\text{V}_2\text{O}_5$ (mg)</th>
<th>Pt (mg)</th>
<th>BET (m$^2$/g monolith)</th>
<th>Dispersion CO/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>827</td>
<td>-</td>
<td>15.4</td>
<td>133</td>
<td>0.29; 0.30; 0.30</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>857</td>
<td>-</td>
<td>17.5</td>
<td>77</td>
<td>0.08; 0.07; 0.07</td>
</tr>
<tr>
<td>Pt/V$_2$O$_5$/TiO$_2$</td>
<td>807</td>
<td>40</td>
<td>17.6</td>
<td>68</td>
<td>-</td>
</tr>
</tbody>
</table>

The Pt/TiO$_2$ sample shows the highest activity for NO oxidation, followed by the Pt/Al$_2$O$_3$ catalyst and the Pt/V$_2$O$_5$/TiO$_2$ sample shows the lowest activity. While Pt/TiO$_2$ and Pt/Al$_2$O$_3$ show a decrease in conversion to NO$_2$ with the time, the NO$_2$ response obtained over Pt/V$_2$O$_5$/TiO$_2$ is stable but on a lower level. This deactivation is also seen in figures 2–4, where the inlet concentrations are the same (600 ppm NO and 8% O$_2$) during the first 60 min of the experiments.

From table 1 it is seen that the Pt dispersion is lower for the Pt/TiO$_2$ catalyst when compared to the Pt/Al$_2$O$_3$ catalyst and that the BET surface area decreases in the order Pt/Al$_2$O$_3$ > Pt/TiO$_2$ > Pt/V$_2$O$_5$/TiO$_2$. The lower BET area of the Pt/TiO$_2$ sample may be the reason for the low platinum dispersion. The platinum dispersion is important for the NO oxidation, increasing the size of the platinum particles increases the NO oxidation activity [9,10] and this can explain the high activity for the Pt/TiO$_2$ sample. For the vanadium containing catalyst no platinum dispersion, see table 1, could be determined due to the interference of vanadium. Thus, it is not possible to rule out the effect of the Pt dispersion on the NO oxidation reaction over this catalyst.

The NO oxidation activity decreases with time for the Pt/Al$_2$O$_3$ and Pt/TiO$_2$ sample, as described above. In a previous study by Olsson and Fridell [9] this type of
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Effect of support on NO oxidation - Influence of C₃H₆ at 200°C

Experimental conditions for sulphur influence of NO oxidation on Pt/Al$_2$O$_3$

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%O$_2$+30ppm SO$_2$ for 22h
   (v) 250°C: 630ppmNO+8%O$_2$ for 30 min
5. NO oxidation exp.
6. Measure platinum dispersion with CO TPD
Influence of SO$_2$ on NO oxidation over Pt/Al$_2$O$_3$ 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$^{-1}$
Influence of SO$_2$ on NO oxidation on Pt/Al$_2$O$_3$

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%

Influence of SO$_2$ on NO oxidation over Pt/Al$_2$O$_3$ 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$^{-1}$
Influence of SO\textsubscript{2} on NO oxidation on Pt/Al\textsubscript{2}O\textsubscript{3}

**Feed mixture:**
- 630 ppm NO and 8 % O\textsubscript{2},
- 5 °C/min
- SV= 39 000 h\textsuperscript{-1}

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

• NO oxidation decreases with time over Pt/Al₂O₃, 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/TiO₂, made the catalyst more stable. Although with a lower activity. Vanadia is acidic.
• SO₂ initially deactivates the NO oxidation on Pt/Al₂O₃
• After about 2h with NO+O₂+SO₂, the activity slowly increases
• After 22h of NO+O₂+SO₂ exposure at 250°C, the catalyst was regenerated and NO oxidation activity increased significantly.
• The Pt dispersion had decreased from 12 to 3.5%
• SO₂ induces Pt sintering already at 200 and 250°C
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