Sulfur Storage and Release over a Diesel Oxidation Catalyst: The Different Deactivation Impacts of $\text{SO}_2$, $\text{SO}_3$ and $\text{H}_2\text{SO}_4$

Tayebeh Hamzehlouyan

Department of Chemical and Petroleum Engineering
Sharif University of Technology, Iran

ETH-Conference on Combustion Generated Nanoparticles

June 20, 2018
Overview

1. Motivation
2. Experimental set up
3. SO₂ oxidation on diesel oxidation catalyst
4. SO₂ adsorption-desorption on a Pt/γ-Al₂O₃ catalyst
5. Sulfur impact on NO oxidation on the catalyst
6. Different deactivation impacts of SO₂, SO₃ and H₂SO₄
7. Conclusions
Motivation

- The relative amounts of SO\textsubscript{2} and SO\textsubscript{3} over a Pt/Al\textsubscript{2}O\textsubscript{3} DOC?
- Different forms of sulfur can have different impacts on DOCs
**Sulfur impact on emissions**

- PM emissions decreases due to oxidation of soluble organic fraction (SOF)
- At 450°C, an overall increase in total PM emission due to **sulfate formation**
- Sulfur can lead to catalyst deactivation
- The aftertreatment catalyst performance is adversely impacted by sulfur

Feed: 20 ppm SO₂, 1%CO, 10% O₂

https://www.dieselnet.com

Bench-scale reactor set up

Feed gas

Water injection system

SO₃ reactor

: On/Off Valve
: Needle Valve
: Mass flow controller
: Pressure Gauge
: Three way diverting valve
: Pressure relief valve
: Filter
Bench-scale reactor set up

Prof. Bill Epling’s lab, University of Houston, TX
Catalyst and reactor tests

- **Catalyst**
  
  γ-Al$_2$O$_3$ and Pt/γ-Al$_2$O$_3$ - supplied by JMI

- **Reactor set up**

- **Analyzer**
  MKS MG-2030 FTIR for gas-phase analysis
  ZnSe windows and MgF$_2$-coated mirrors
SO₂ oxidation on diesel oxidation catalyst

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3 \]

- Reaction mechanism

\[
\begin{align*}
\text{SO}_2 + * & \xleftrightarrow{1,2} \text{SO}_2^* \\
\text{O}_2 + 2* & \xleftrightarrow{3,4} 2\text{O}^* \\
\text{SO}_2^* + \text{O}^* & \xleftrightarrow{5,6} \text{SO}_3^* \\
\text{SO}_3^* & \xleftrightarrow{7,8} \text{SO}_3 + *
\end{align*}
\]

Feed: SO₂: 149 ppm  SO₃:106 ppm  O₂:10%

Hamzehlouyan et al.; Applied Catalysis B: Environmental 152 (2014) 108
**SO₂ adsorption-desorption tests**

- Alumina effect is significant on the SO₂ storage/release on Pt/γ-Al₂O₃
- Pt enhances the contribution of the more stable species

<table>
<thead>
<tr>
<th>SO₂ loading in washcoat</th>
<th>γ-Al₂O₃</th>
<th>2.3 μmol/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/γ-Al₂O₃</td>
<td></td>
<td>2.5 μmol/m²</td>
</tr>
</tbody>
</table>

- 48 ppm
- 157°C
- 925°C
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

- Thermo Scientific Nicolet 6700 FT-IR
- Harrick Scientific praying mantis

- *In situ* characterization of surface intermediates under reaction dynamics
- At 150°C, molecularly adsorbed SO$_3$ and sulfites form on Pt/Al$_2$O$_3$
- At 400°C, surface sulfates are dominant
Adsorbed species on $\gamma$-Al$_2$O$_3$ and Pt/$\gamma$-Al$_2$O$_3$

SO$_2$-S1: Molecular SO$_2$ on Al sites
SO$_2$-S2: Surface sulfite
SO$_2$-S3: Surface sulfate
SO$_2$-S4: Bulk Al$_2$(SO$_4$)$_3$

Hamzehlouyan et al.; *Applied Catalysis B: Environmental* 181 (2016) 587
NO oxidation in the presence of SO$_2$ and SO$_3$

- NO oxidation is significantly inhibited in the presence of sulfur oxides
- At $T \geq 250^\circ C$, SO$_2$ oxidation becomes important

NO: 405 ppm, O$_2$: 5%, balanced with N$_2$

SV = 25000 h$^{-1}$, Total flow = 3.55 L/min
Different impacts of SO$_2$, SO$_3$ and H$_2$SO$_4$

**Treatment Procedure**

- **SO$_2$**: 50 ppm SO$_2$ at 240°C overnight
- **SO$_3$**: 77 ppm SO$_3$ at 240°C for 2 h and in the feed
- **H$_2$SO$_4$**: 50 ppm H$_2$SO$_4$, 2% water, 10% O$_2$ at 150°C for 24 h

**Results:**

- S inhibition effect on Pt/$\gamma$-Al$_2$O$_3$: 
  - H$_2$SO$_4$ > SO$_3$ > SO$_2$

Hamzehlouyan et al.; *Topics in Catalysis* 59 (2016) 1028
Conclusions

- The kinetic model for SO$_2$ oxidation can predict relative amounts of SO$_2$ and SO$_3$ at different temperatures.
- SO$_2$ adsorption study showed significant effect of catalyst support in sulfur storage.
- Multiple sulfur species on diesel oxidation catalyst were identified.
- **Sulfur uptake on Pt/γ-Al$_2$O$_3$** upon exposure to different forms of sulfur: H$_2$SO$_4$ > SO$_3$ > SO$_2$.
- Deactivation impact of different sulfur species: H$_2$SO$_4$ > SO$_3$ > SO$_2$.
Acknowledgements

University of Houston
Dr. Bill Epling
Dr. Chaitanya Sampara

Cummins, Inc.
Dr. Aleksey Yezerets
Dr. Junhui Li
Dr. Ashok Kumar

MKS Instruments, Inc.
Dr. Barbara Marshik
Sylvie Bosch-Charpenay
Bill Murphy

Johnson Matthey
Dr. Howard Hess
SO$_2$ Oxidation: Experimental Study

SO$_2$ + $\frac{1}{2}$O$_2$ $\leftrightarrow$ SO$_3$

$(-r_{SO_2}) = k[SO_2]^\alpha[O_2]^\beta[SO_3]^\gamma$

SO$_3$ Inhibition effect

SO$_2$ : 52-310 ppm  SO$_3$ : 58-259 ppm  O$_2$ : 5-15%
SO$_2$ oxidation: Modeling results

Temperature (°C)

Surface coverage at channel outlet

<table>
<thead>
<tr>
<th>Temp.</th>
<th>RDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>T ≤ 300°C</td>
<td>Surface reaction and O$_2$ adsorption</td>
</tr>
<tr>
<td>T &gt; 300°C</td>
<td>Surface reaction</td>
</tr>
</tbody>
</table>

Feed: SO$_2$: 149 ppm  SO$_3$: 106 ppm  O$_2$: 10%
SO₂ impact on CO oxidation

• Two CO TPO runs were conducted back to back after SO₂ saturation.

• No significant change was observed in the CO oxidation activity.

• The sulfur species are in a stable state on the catalyst.

SO₂ treatment: 50 ppm SO₂ at 220°C for 3 h
SO₂ impact on NO oxidation

- NO oxidation activity of Pt/γ-Al₂O₃ was tested after SO₂ saturation.
- During the NO oxidation cycles, no significant change occurs on the active sites involved in the reaction.
- Upon SO₂ adsorption, stable sulfur species are formed on the catalyst.

**SO₂ treatment:** 50 ppm SO₂ at 220°C for 3 h

**SO₂ co-feeding:** 38 ppm SO₂ in the feed
Comparison with the SAE paper

- NO oxidation activity was substantially recovered after baking, due to the sulfur migration from PGM to support.

- Catalyst “Baking”: Heating at 400°C with 5% O₂ to redistribute sulfur.

- Freshly-deposited SO₂ is associated with the active sites.

Junhui Li et al., SAE (2013)

Time effect not significant at 400°C.
Kinetic model for $\text{SO}_2$ adsorption-desorption

- Adsorption mechanism

\[\text{SO}_2 + S1 \rightleftharpoons_{1,2} \text{SO}_2 - S1\]
\[\text{SO}_2 + S2 \rightleftharpoons_{3,4} \text{SO}_2 - S2\]
\[\text{SO}_2 + S3 \rightleftharpoons_{5,6} \text{SO}_2 - S3\]
\[\text{SO}_2 - S3 + S4 \rightleftharpoons_{7,8} \text{SO}_2 - S4 + S3\]

$\gamma$-Al$_2$O$_3$

Adsorption conditions:
$\text{SO}_2=48$ ppm  $T=157^\circ\text{C}$
Model predictions

Surface coverages on Pt/γ-Al₂O₃

\[
\theta_{SO2S1} \quad \theta_{SO2S2} \quad \theta_{SO2S3} \quad \theta_{SO2S4}
\]

\[\text{[SO}_2\text{]} = 50 \text{ ppm}\]

Adsorption T = 160°C

SO₂: Gas phase
SO₂-S1: SO₂-Al
SO₂-S2: Surface sulfite
SO₂-S3: Surface sulfate
SO₂-S4: Bulk Al₂(SO₄)₃

Ultra low S fuel: 15 ppm
\[\text{[SO}_2\text{]} = 1 \text{ ppm}\]

Saturation time ≈ 16 h

Hamzehlouyan et al.; Applied Catalysis B: Environmental 181 (2016) 587