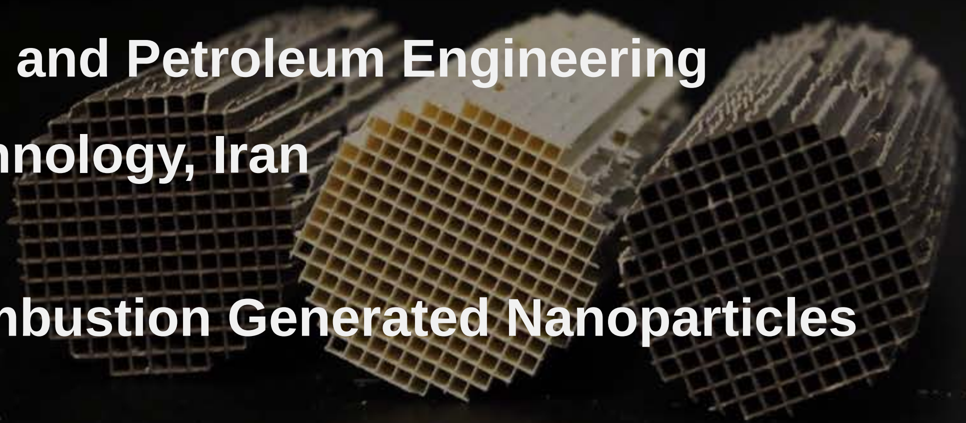
Sulfur Storage and Release over a Diesel Oxidation Catalyst: The Different Deactivation Impacts of SO_2, SO_3 and H_2SO_4

Tayebeh Hamzehlouyan

Department of Chemical and Petroleum Engineering

Sharif University of Technology, Iran



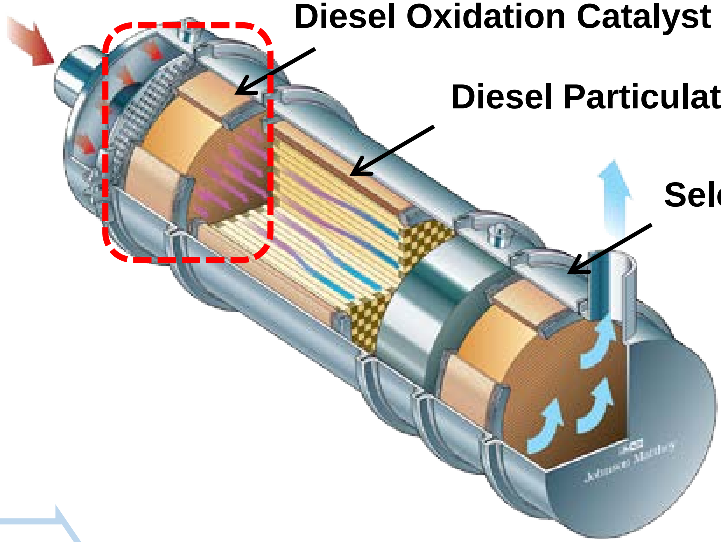
ETH-Conference on Combustion Generated Nanoparticles

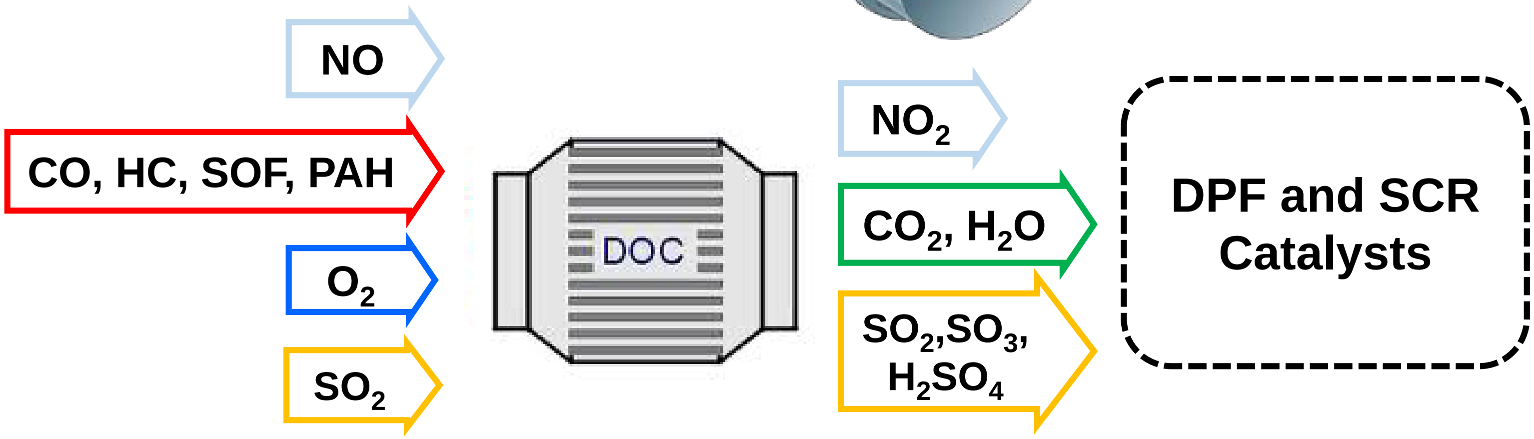
June 20, 2018

Overview

1. Motivation
2. Experimental set up
3. SO_2 oxidation on diesel oxidation catalyst
4. SO_2 adsorption-desorption on a Pt/γ-Al_2O_3 catalyst
5. Sulfur impact on NO oxidation on the catalyst
6. Different deactivation impacts of SO_2, SO_3 and H_2SO_4
7. Conclusions

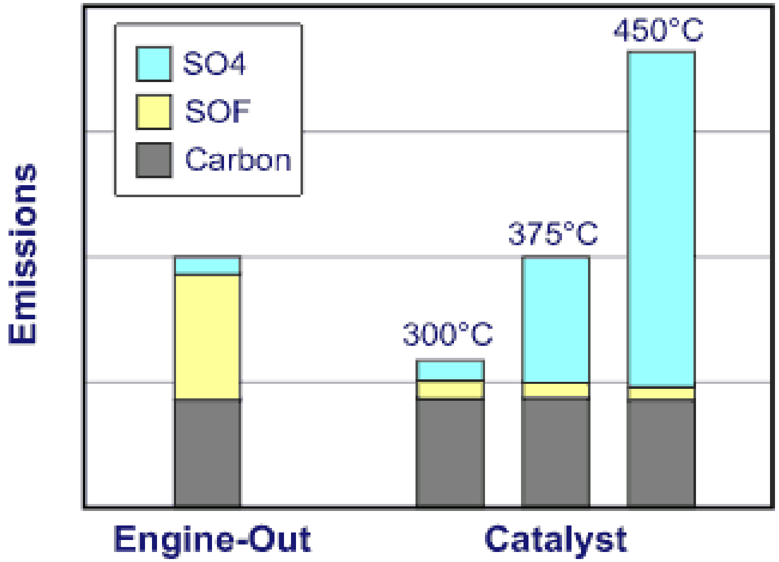
Motivation





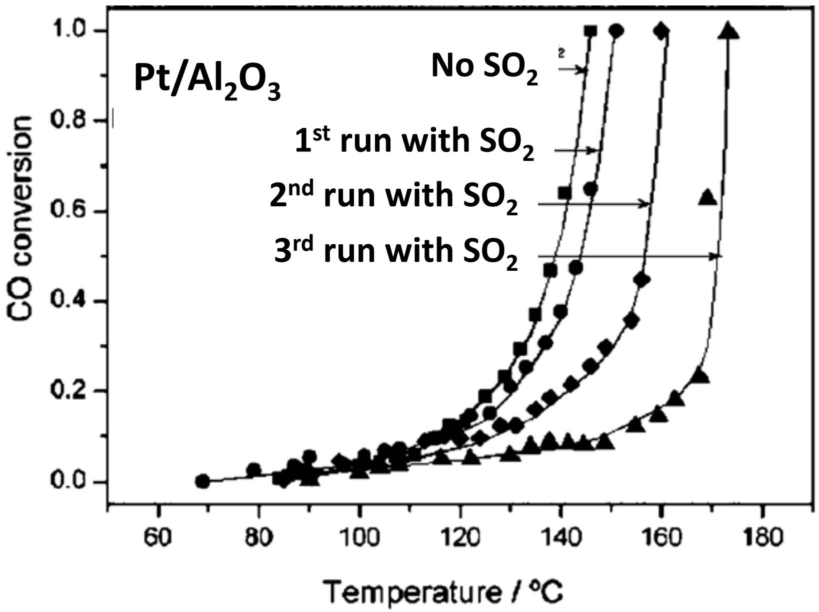
- The relative amounts of SO_2 and SO_3 over a Pt/Al_2O_3 DOC?
- Different forms of sulfur can have different impacts on DOCs

Sulfur impact on emissions



https://www.dieselnet.com

Feed: 20 ppm SO_2, 1%CO, 10% O_2

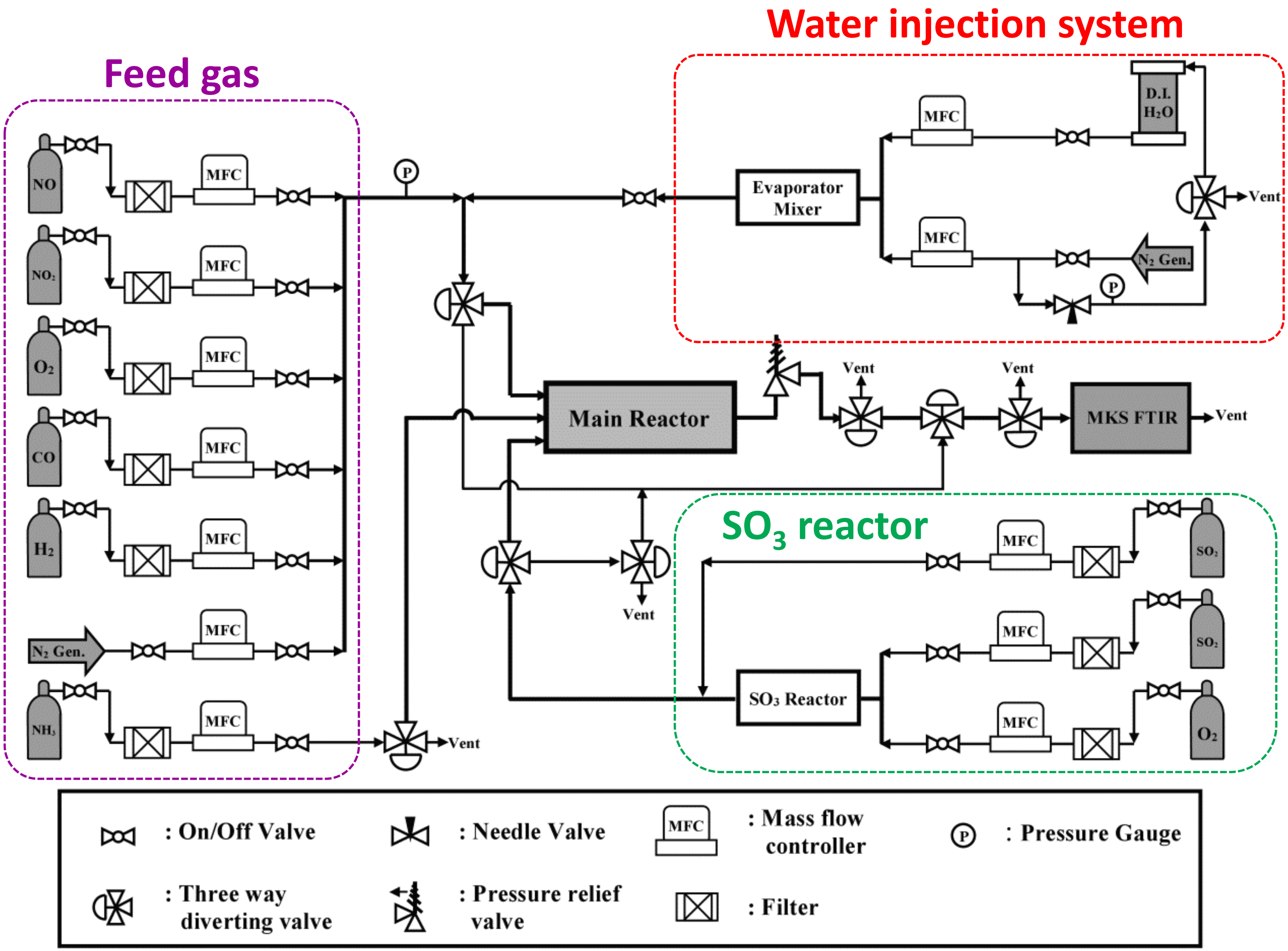


Gracia et al., *J. Catal.* 233 (2005) 372

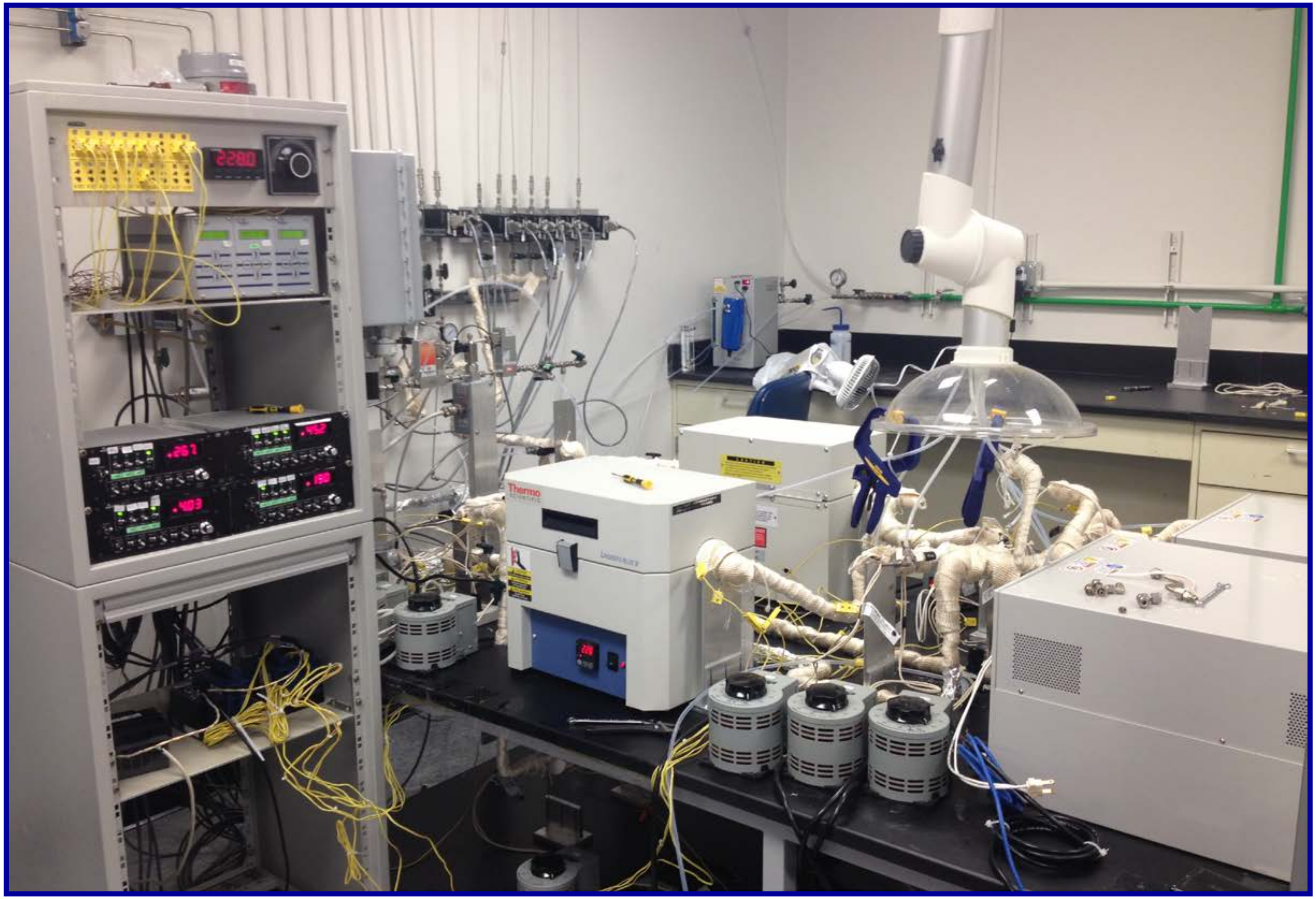
- PM emissions decreases due to oxidation of soluble organic fraction (SOF)
- At 450°C, an overall increase in total PM emission due to **sulfate formation**

- Sulfur can lead to catalyst deactivation
- The aftertreatment catalyst performance is adversely impacted by sulfur

Bench-scale reactor set up

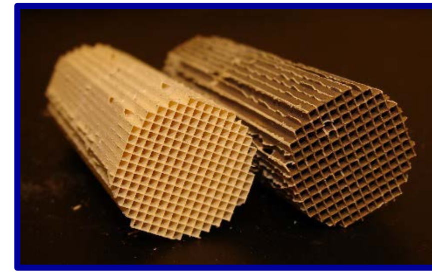


Bench-scale reactor set up



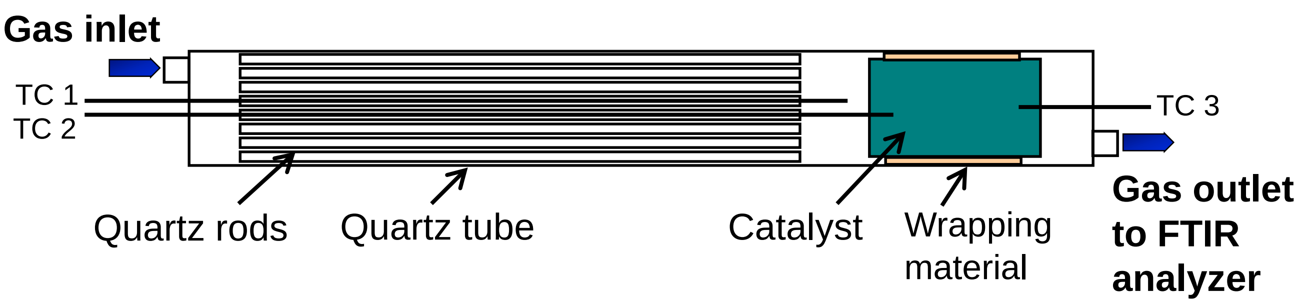
Prof. Bill Epling's lab, University of Houston, TX

Catalyst and reactor tests

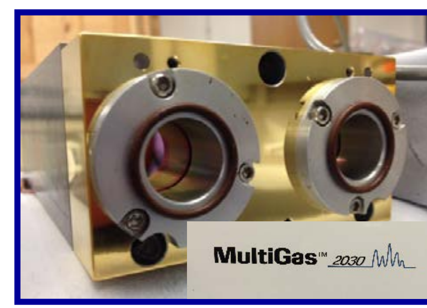


- **Catalyst**

  γ-Al_2O_3 and Pt/γ-Al_2O_3 - supplied by JMI



- **Reactor set up**



- **Analyzer**

  MKS MG-2030 FTIR for gas-phase analysis

  ZnSe windows and MgF_2-coated mirrors

SO_2 oxidation on diesel oxidation catalyst

$$SO_2 + \frac{1}{2} O_2 \leftrightarrow SO_3$$

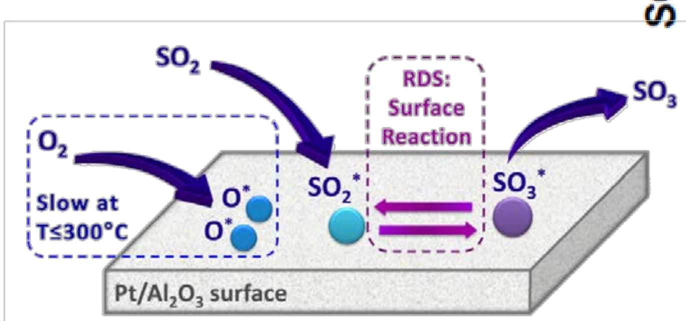
- **Reaction mechanism**

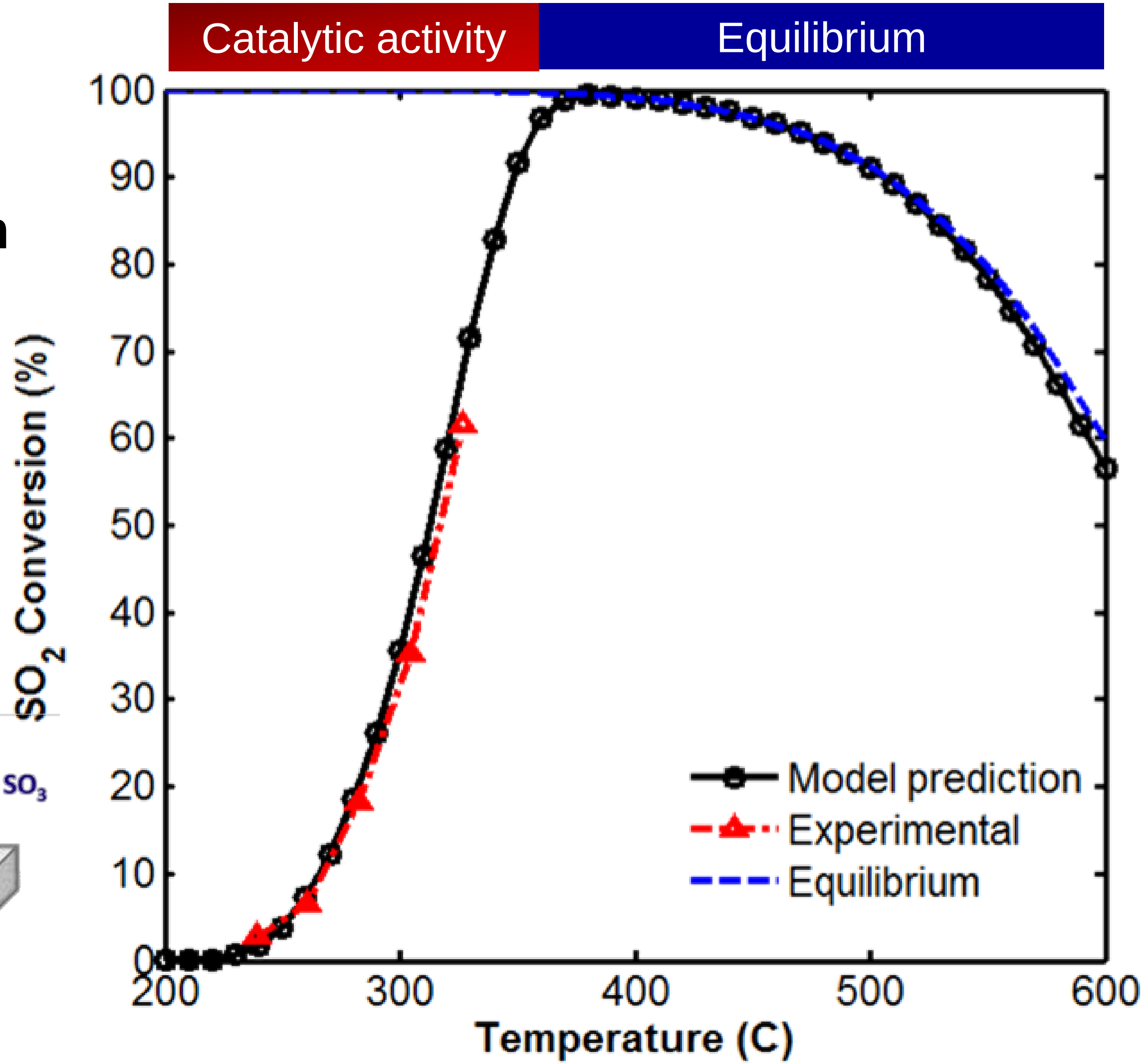
$$SO_2 + * \xleftrightarrow{1,2} SO_2^*$$

$$O_2 + 2* \xleftrightarrow{3,4} 2O^*$$

$$SO_2^* + O^* \xleftrightarrow{5,6} SO_3^*$$

$$SO_3^* \xleftrightarrow{7,8} SO_3 + *$$

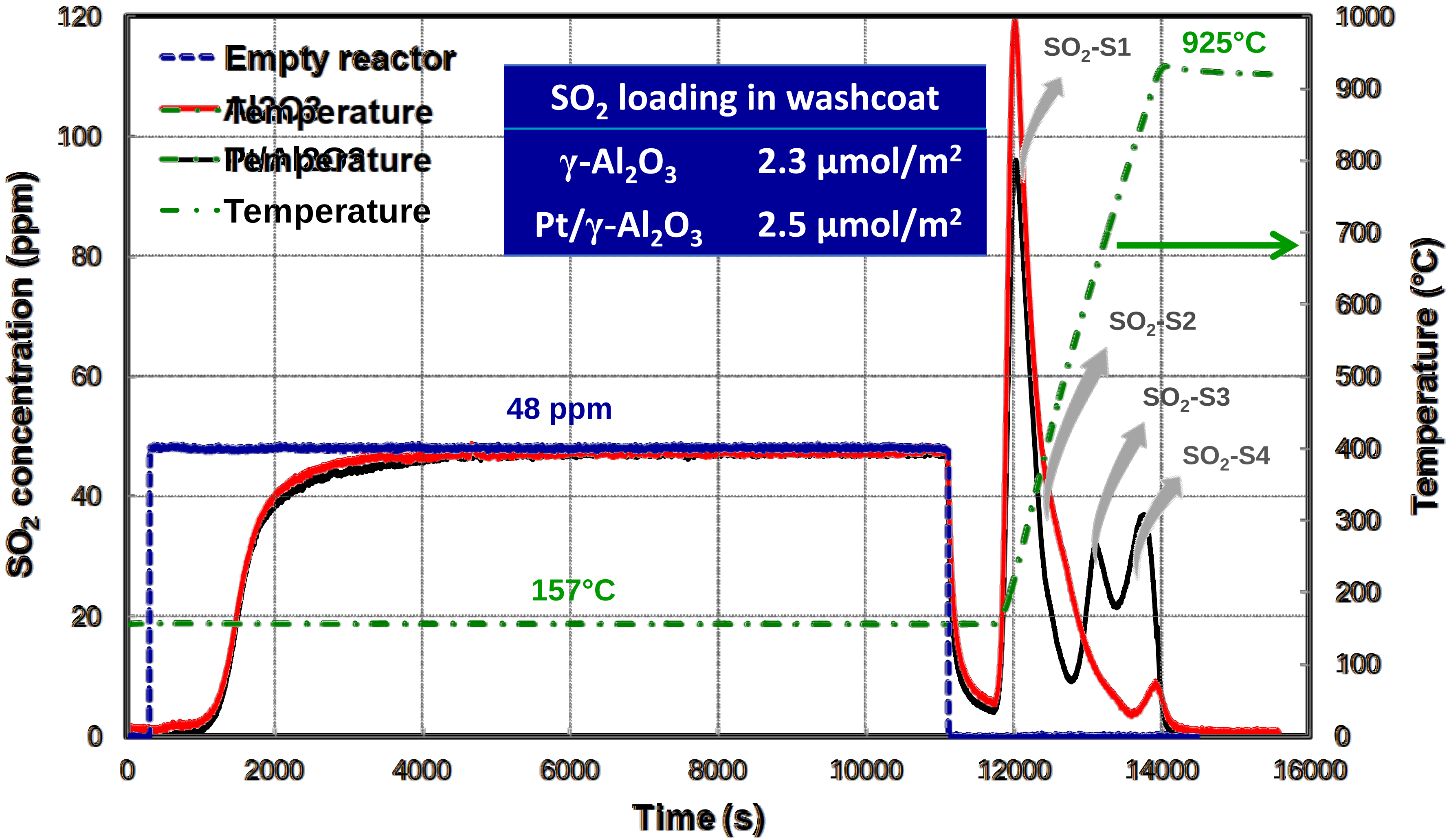




Feed: SO_2: 149 ppm SO_3:106 ppm O_2:10%

Hamzehlouyan et al.; *Applied Catalysis B: Environmental* 152 (2014) 108

SO_2 adsorption-desorption tests

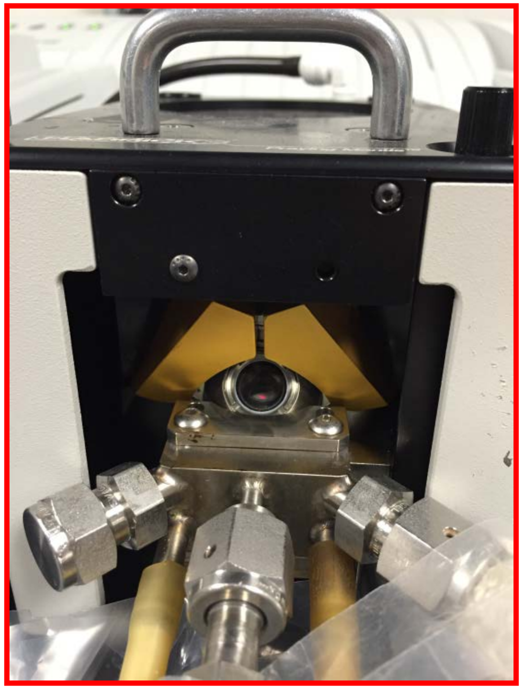


- Alumina effect is significant on the SO_2 storage/release on Pt/γ-Al_2O_3
- Pt enhances the contribution of the more stable species

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

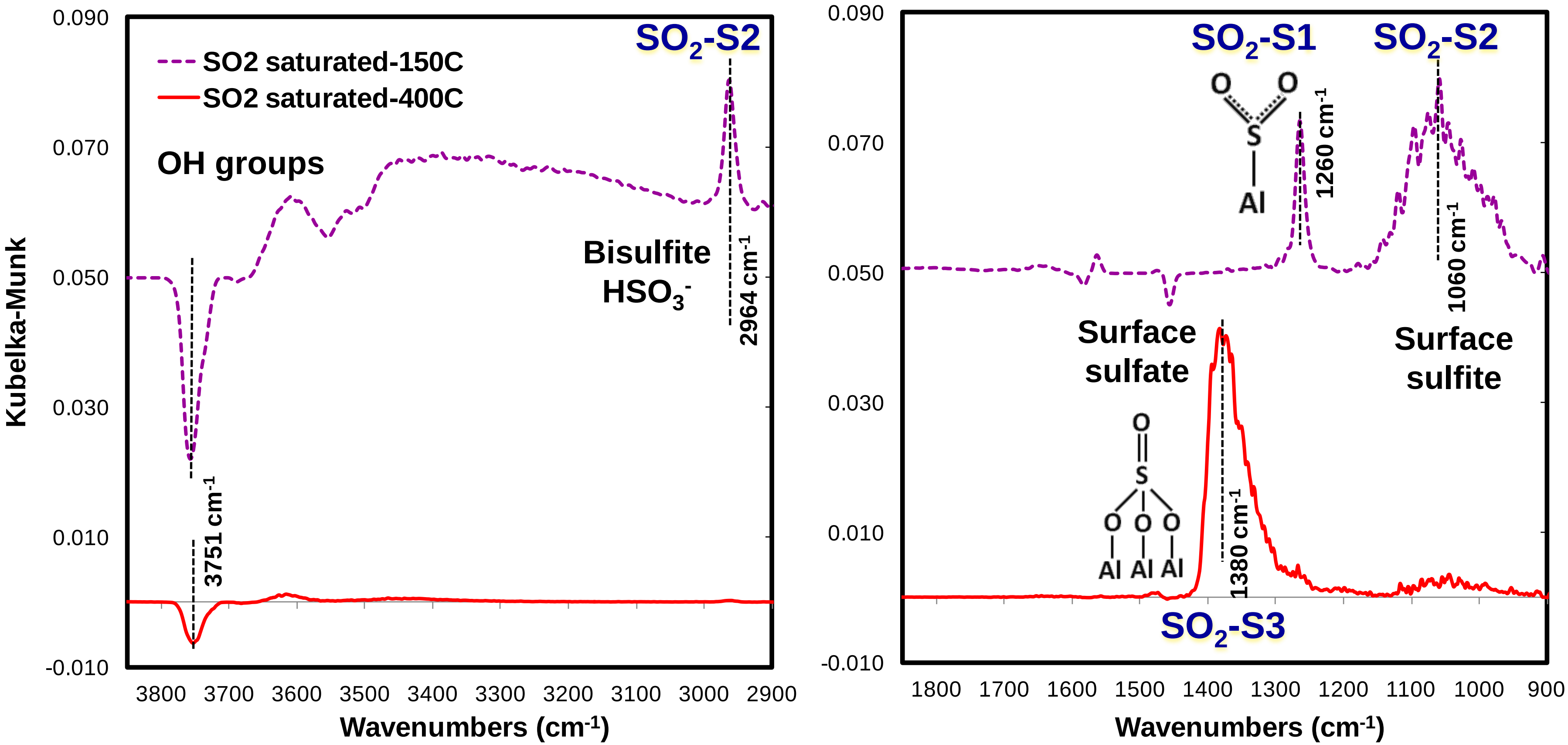
Thermo Scientific Nicolet 6700 FT-IR

Harrick Scientific praying mantis



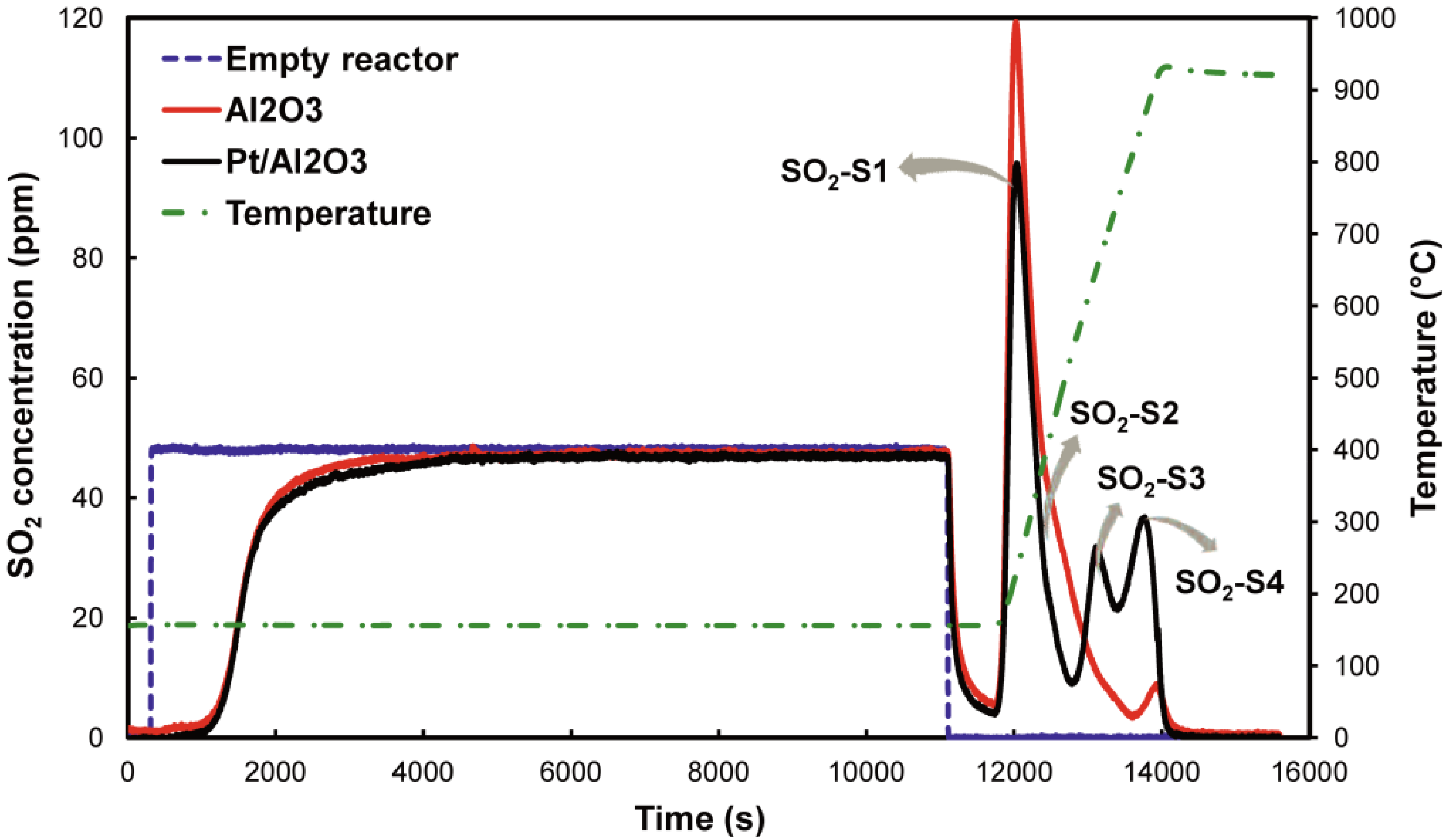
- ***In situ* characterization of surface intermediates under reaction dynamics**

DRIFTS study of SO_2 adsorption on Pt/γ-Al_2O_3

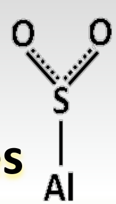


- At 150°C, molecularly adsorbed SO_3 and sulfites form on Pt/Al_2O_3
- At 400°C, surface sulfates are dominant

Adsorbed species on γ-Al_2O_3 and Pt/γ-Al_2O_3



SO_2-S1:
Molecular
SO_2 on Al sites



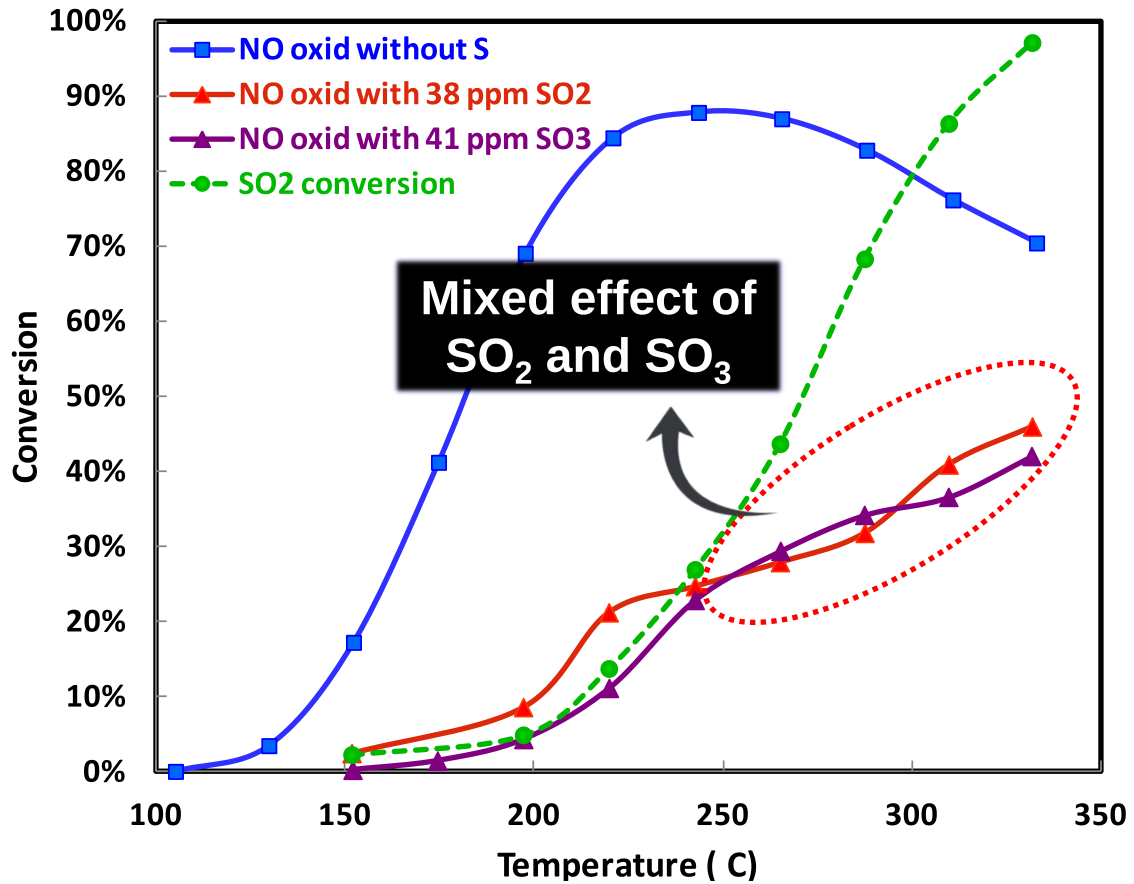
SO_2-S2:
Surface sulfite

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

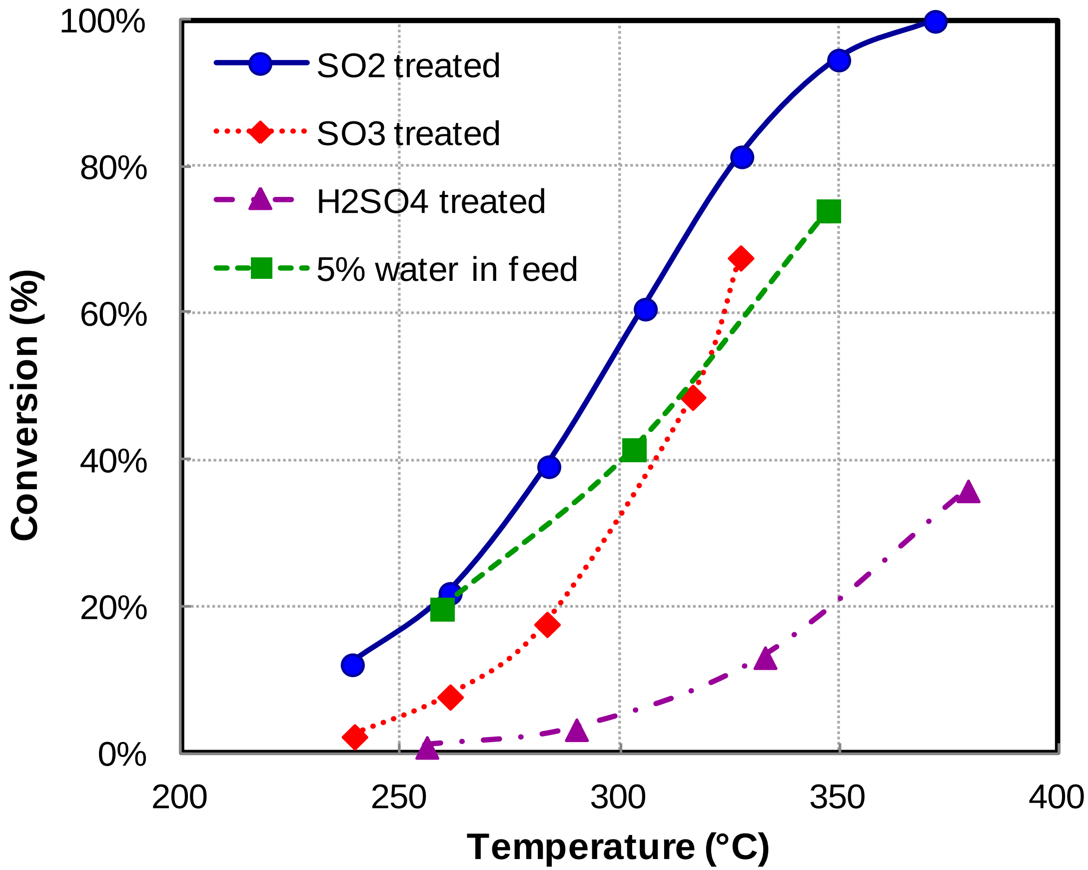


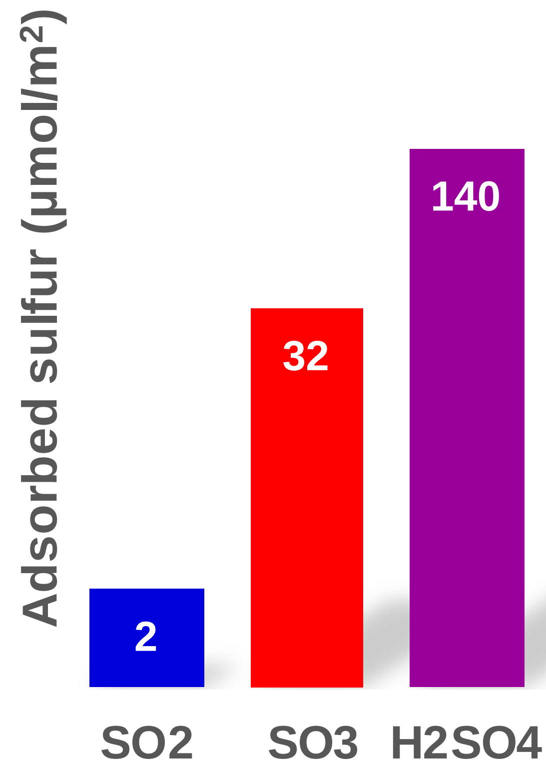
NO: 405 ppm, O_2: 5%, balanced with N_2

SV = 25000 h^{-1}, Total flow = 3.55 L/min

- NO oxidation is significantly inhibited in the presence of sulfur oxides
- At T ≥ 250°C, SO_2 oxidation becomes important

Different impacts of SO_2, SO_3 and H_2SO_4





Treatment	Procedure
SO_2	…t
SO_3	…he feed
H_2SO_4	50 ppm H_2SO_4, 2% water, 10% O_2 at 150°C for 24 h

S inhibition effect on Pt/γ-Al_2O_3:

H_2SO_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_2O_3** upon exposure to different forms of sulfur: $H_2SO_4 > SO_3 > SO_2$
- Deactivation impact of different sulfur species: **$H_2SO_4 > SO_3 > SO_2$**

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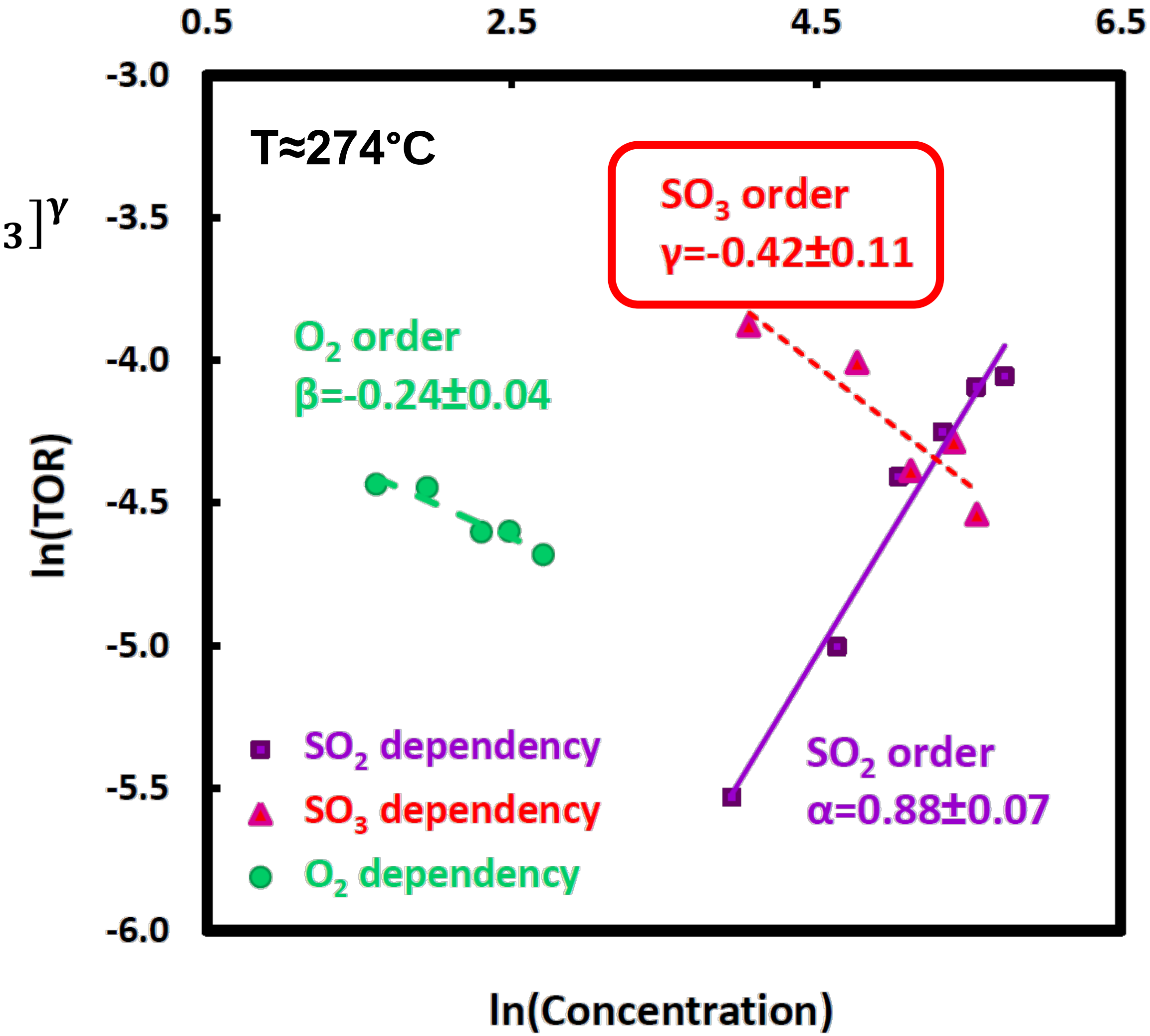
SO_2 Oxidation: Experimental Study

$$SO_2 + \frac{1}{2} O_2 \leftrightarrow SO_3$$

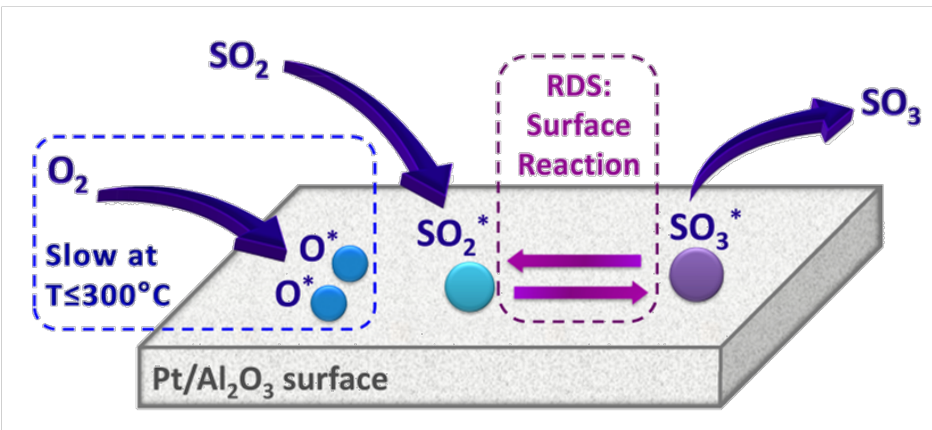
$$(-r_{SO_2}) = k[SO_2]^{\alpha}[O_2]^{\beta}[SO_3]^{\gamma}$$

SO_3 Inhibition effect



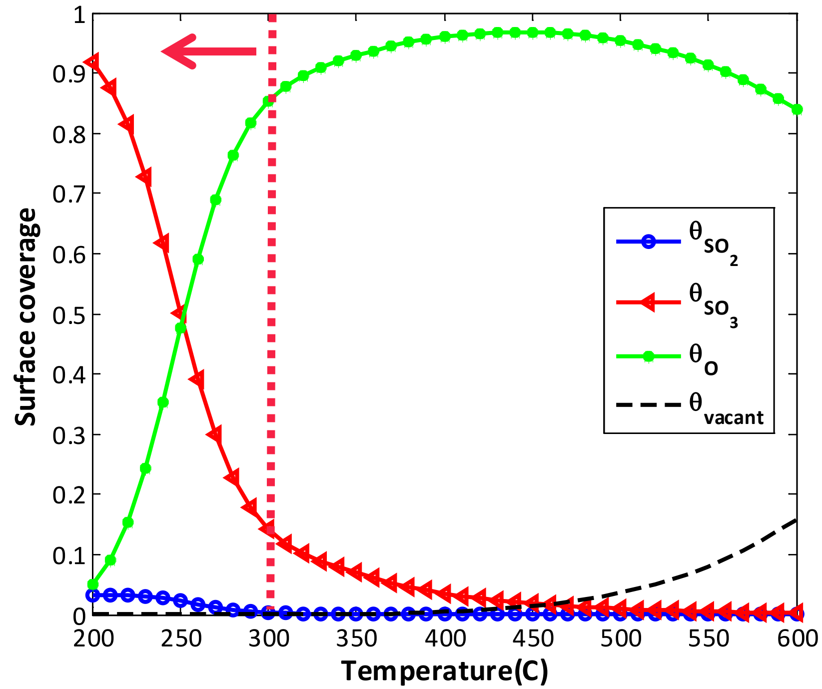
SO_2 : 52-310 ppm SO_3: 58-259 ppm O_2: 5-15%

SO_2 oxidation: Modeling results



Temp.	RDS
T ≤ 300°C	Surface reaction and O_2 adsorption
T > 300°C	Surface reaction

Surface coverage at channel outlet



Feed: SO_2: 149 ppm SO_3:106 ppm O_2:10%

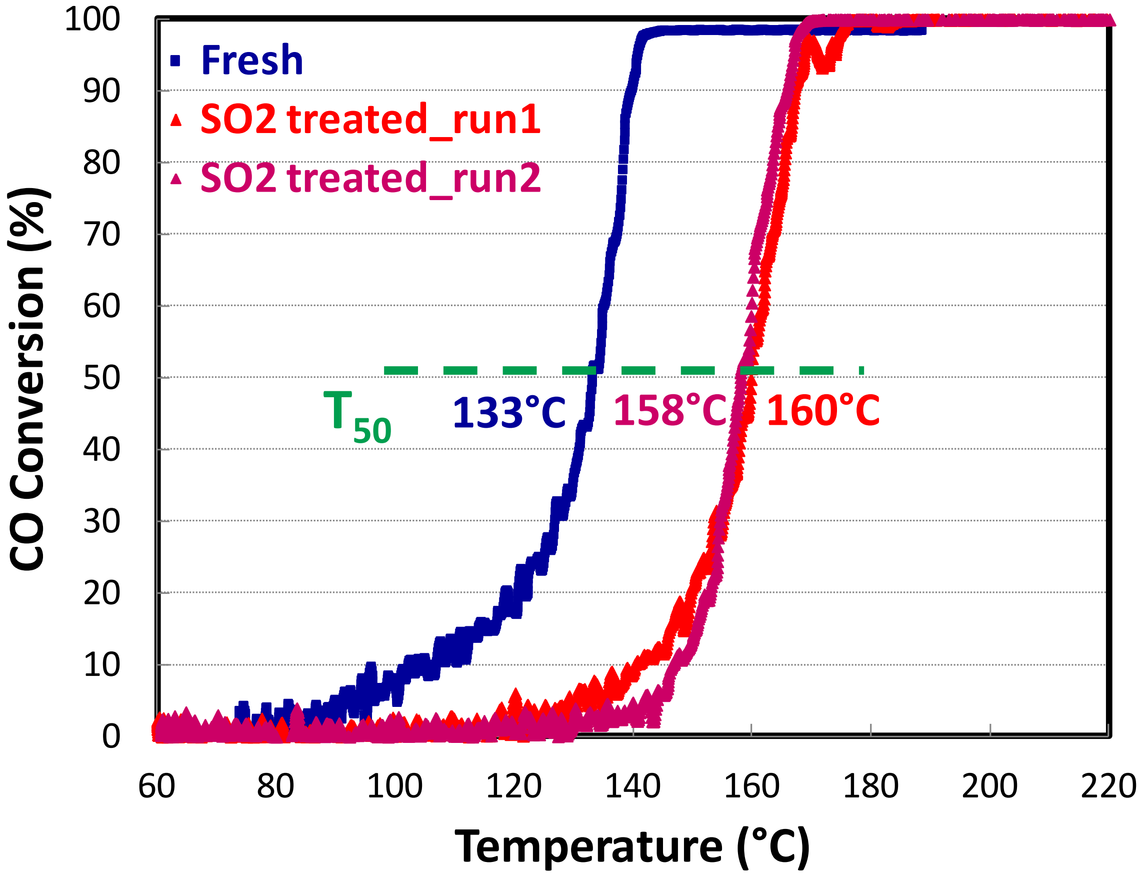
Hamzehlouyan et al.; *Applied Catalysis B: Environmental* 152 (2014) 108

SO_2 impact on CO oxidation

- Two CO TPO runs were conducted back to back after SO_2 saturation.
- No significant change was observed in the CO oxidation activity.
- The **sulfur species are in a stable state** on the catalyst.

CO: 513 ppm, O_2: 5%, balanced with N_2

SV = 50000 h^{-1}, Ramp rate = 10°C/min



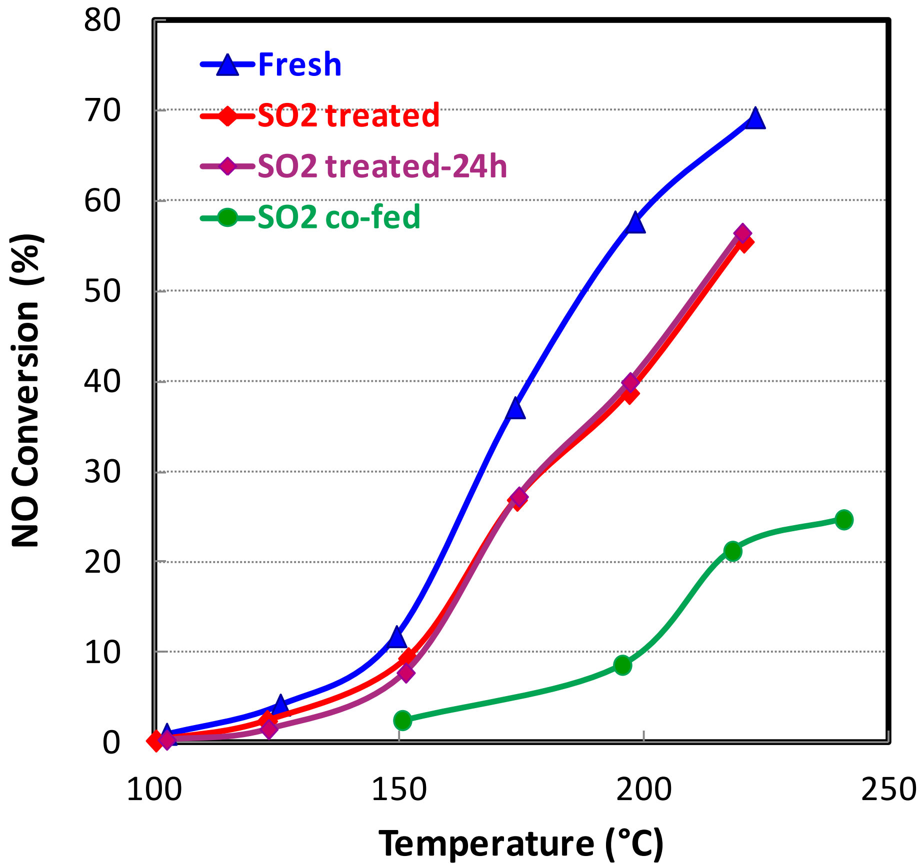
SO_2 treatment: 50 ppm SO_2 at 220°C for 3 h

SO_2 impact on NO oxidation

- NO oxidation activity of Pt/γ-Al_2O_3 was tested after SO_2 saturation.
- During the NO oxidation cycles, no significant change occurs on the active sites involved in the reaction.
- Upon SO_2 adsorption, stable sulfur species are formed on the catalyst.

NO: 320 ppm, O_2: 5%, balanced with N_2

SV = 50000 h^{-1}, Total flow = 5.28 L/min



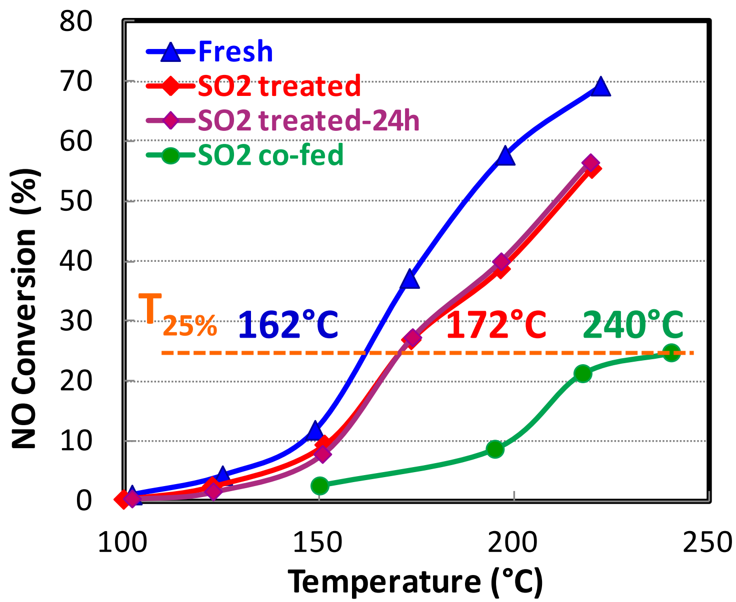
SO_2 treatment: 50 ppm SO_2 at 220°C for 3 h

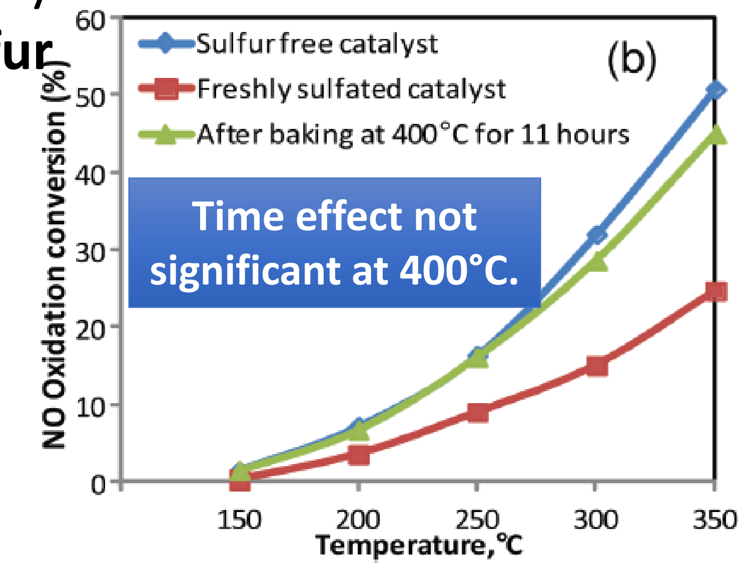
SO_2 co-feeding: 38 ppm SO_2 in the feed

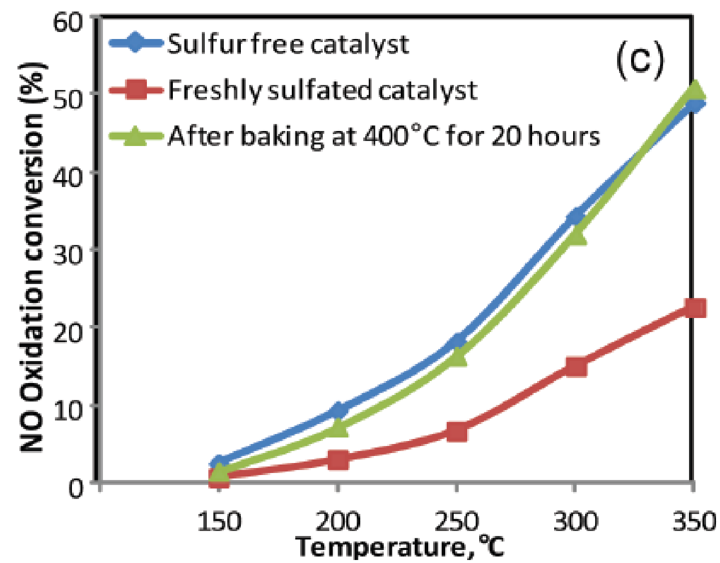
Comparison with the SAE paper

- 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% O_2 to redistribute sulfur**.

- **Freshly-deposited SO_2 is associated with the active sites.**







Junhui Li et al., SAE (2013)

Kinetic model for SO_2 adsorption-desorption

- **Adsorption mechanism**

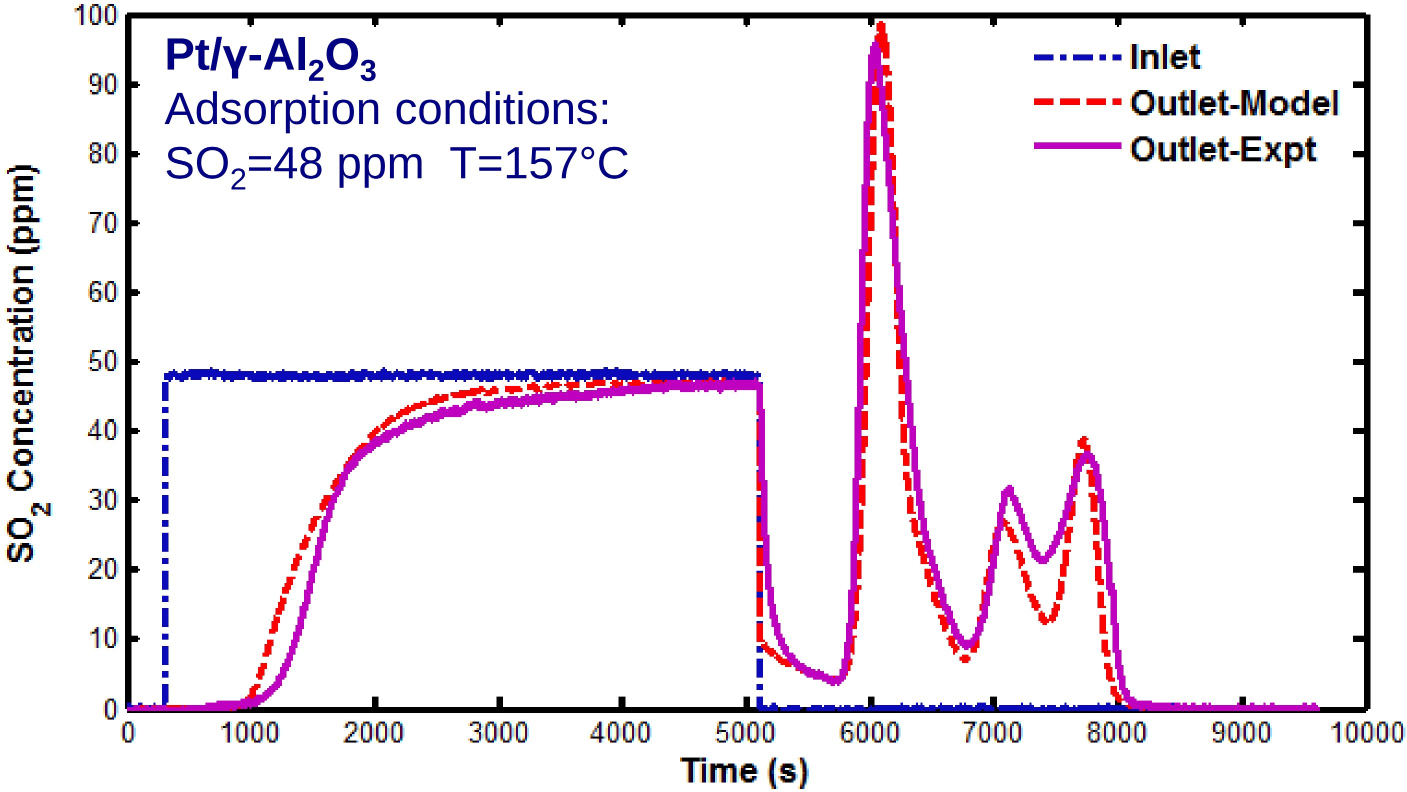
$$SO_2 + S1 \xleftrightarrow{1,2} SO_2 - S1$$

$$SO_2 + S2 \xleftrightarrow{3,4} SO_2 - S2$$

$$SO_2 + S3 \xleftrightarrow{5,6} SO_2 - S3$$

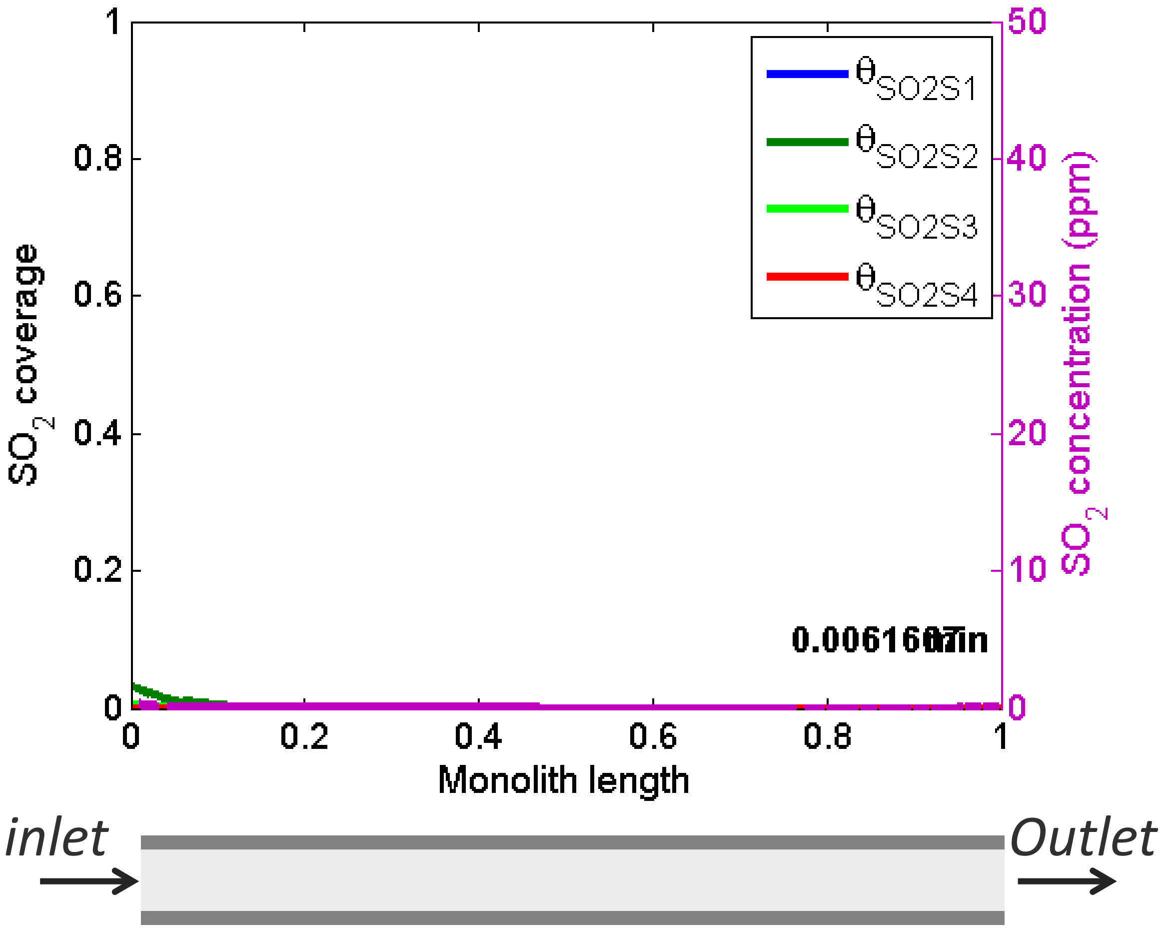
$$SO_2 - S3 + S4 \xleftrightarrow{7,8} SO_2 - S4 + S3$$

$$x_{SO_2}(z,t) \qquad \theta_{SO_2 - Si}(z,t)$$



Model predictions

Surface coverages on Pt/γ-Al_2O_3



$[SO_2]$ = 50 ppm

Adsorption T = 160°C

SO_2:	Gas phase
SO_2-S1:	SO_2-Al
SO_2-S2:	Surface sulfite
SO_2-S3:	Surface sulfate
SO_2-S4:	Bulk $Al_2(SO_4)_3$

Ultra low S fuel: 15 ppm

$[SO_2]$ = 1 ppm

Saturation time ≈ 16 h

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